Journal of Radioanalytical and Nuclear Chemistry (2020) 324:169–188
https://doi.org/10.1007/s10967-020-07053-4

Reference materials for quality assurance of environmental plutonium analysis

Junwen Wu[1] **· Jian Zheng**[2]

Received: 26 October 2019 / Published online: 22 February 2020

Abstract
Reference materials (RMs) are very important for method development and validation. In order to quickly and reliably select the suitable RM for validating the determination of plutonium (Pu), we reviewed the RMs of Pu and prepared extensive Pu datasets in this study. After data treatment and a series of statistical analyses, we obtained the statistical values of $^{238-241}$Pu activity and Pu isotopic ratio for RMs. The statistical value of $^{239+240}$Pu activity is consistent with the certified value, indicating these measured values are highly reliable. We anticipate that, after further independent work at different laboratories, the statistical values of the Pu isotopic ratios are very important to validate analysis methods and calibrate the mass bias for environmental Pu analysis.

Keywords Reference material · Plutonium · Pu isotopic ratios · Environmental samples · Statistical value

Introduction

Plutonium (Pu), an anthropogenic radionuclide, has been intentionally or accidentally introduced into the environment since the first nuclear weapons tests in the mid-1940s through various human activities including: releases in accidents (e.g., Chernobyl and Fukushima [1, 2]); discharges from reprocessing plants [3–5]; and global fallout from above-ground nuclear weapons testing [6, 7]. Because of their high chemical toxicity, long half-lives and internal radiation threat, the determination of concentrations of Pu isotopes in the environment is of great important. Meanwhile, Pu isotopes in the environment have been widely used as tracers to study environmental processes [8], such as water circulation and scavenging efficiency in the oceans [9–13]. All such investigations require highly sensitive analytical techniques to measure Pu isotopic compositions [14], producing high quality data sets.

Initially, α-spectrometry was used as the main analytical tool to determine Pu concentration in the environment for the alpha emitting isotopes (^{238}Pu, ^{239}Pu and ^{240}Pu) [15, 16]. However, α-spectrometry is burdened with several disadvantages such as requiring a large volume of sample, laborious pretreatment and long counting time ranging from days to several weeks. Also, α-spectrometry has no ability to distinguish ^{239}Pu and ^{240}Pu due to their nearly identical α radiation energies (5.16 MeV and 5.17 MeV, respectively). Thus, α-spectrometry cannot provide information on the ^{240}Pu/^{239}Pu atom ratio, which hampers Pu tracing studies of environmental processes. The ^{240}Pu/^{239}Pu atom ratio is related to the Pu contamination source because Pu isotopic ratios vary with reactor type, nuclear fuel burn-up time, neutron flux and energy, and for fallout from nuclear detonations, they vary with weapon type and yield [17]. The average ^{240}Pu/^{239}Pu atom ratio of global fallout is considered to be 0.180 ± 0.014 [18]. Weapons-grade Pu has a lower ^{240}Pu/^{239}Pu atom ratio (0.01–0.07) because of its high ^{239}Pu purity [19, 20]. Reported ^{240}Pu/^{239}Pu atom ratios of reactor-grade Pu vary from 0.2 to 1.0 depending on the fuel burn-up, for example, they are 0.30–0.38 from Fukushima

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10967-020-07053-4) contains supplementary material, which is available to authorized users.

✉ Jian Zheng
zheng.jian@qst.go.jp

Junwen Wu
wujw@stu.edu.cn

1 Institute of Marine Sciences, Shantou University, Shantou 515063, China

2 Department of Radioecology and Fukushima Project, National Institutes for Quantum and Radiological Science and Technology, Anagawa 491, Inage, Chiba 263–8555, Japan

accident fuel [2, 21] and 0.42–0.52 from Chernobyl accident fuel [22–25].

In the past 30 years, thanks to the rapid development of mass spectrometry, various analytical methods for Pu determination have been established in environmental samples, such as thermal ionization mass spectrometry (TIMS [4, 5, 26]), accelerator mass spectrometry (AMS [27]), inductively coupled plasma mass spectrometry (ICP-MS [11, 28–30]) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS [12, 13, 31]). Compared to α-spectrometry, mass spectrometry offers advantages for Pu determination, including high sensitivity, a small sample volume requirement and a capability to provide accurate information about the $^{240}Pu/^{239}Pu$ atom ratio. Certainly, alpha spectrometry cannot be totally replaced by ICP-MS methods, for example, ^{238}Pu can only be measure by alpha spectrometry at the present. The standards of Pu isotopes did not catch up with the developments in mass spectrometric instrumentation and measurement methodologies for the last 30 years [32]. In order to produce consistent and reliable results, laboratories must implement an appropriate quality control/quality assurance (QC/QA) program in which their performance can be monitored. The use of reference materials (RMs) is highly recommended for method development and validation. Meanwhile, confidence in comparability and reliability of measurement results in nuclear materials and environment sample analyses have been established via RMs. Isotopic ratios of Pu in the environment have been widely investigated to elucidate its source terms and to study its behavior and fate [5, 12, 13, 33].

According to the International Organization for Standardization (ISO), RMs have property values certified by technical validations from worldwide inter-comparison exercises traceable to SI units. Pu-RMs, supplied by the National Institute of Standards and Technology (NIST), European Commission Directorate General Joint Research Centre and International Atomic Energy Agency (IAEA), are used in the assay and isotopic standard as the spike in the analysis of Pu by isotope dilution mass spectrometry. The Pu-RMs are designed for use in developing accurate methods of analysis, calibrating measurement systems including determining performance characteristics or measuring a property at the state-of-the-art limit and ensuring long-term adequacy and integrity of measurement quality assurance programs [34]. The following should be considered when Pu-RMs are chosen: (1) the RMs should satisfy the user's target; (2) the matrix and the concentration of Pu-RMs should be as close as possible to the test values of sample: (3) handling and storage should be done according to the certification document; and (4) the Pu-RMs should be used within the validity period. Many matrices, such as sediment, seawater, biota and fallout, of Pu-RMs have been presented in the literature. The activity levels of Pu-RMs are usually certified by the IAEA or NIST. For any certified value and/or information value, one should refer to the original certification of the related RMs. However, the values of Pu isotopic ratio are not always simultaneously certified, for example, the certified $^{239+240}Pu$ activities of IAEA-384 (Fangataufa Lagoon Sediment) and IAEA-385 (Irish Sea Sediment) were given as corresponding to 103–110 Bq kg^{-1} and 2.89–3.00 Bq kg^{-1} at the 95% confidence interval by the IAEA, but their $^{240}Pu/^{239}Pu$ atom ratios were not provided by the agency. Nevertheless, the missing $^{240}Pu/^{239}Pu$ atom ratios of IAEA-384 and IAEA-385 are usually able to be found in the literatures [31, 35–38].

Our objective here is to review the Pu-RMs covering sediment/soil, seawater, biota, and fallout and provide their statistical values of Pu isotopic ratios after statistical analysis of Pu datasets. The certified activity of Pu and accurate information on isotopic ratio of Pu in RMs is important for QC/QA analyses and method validations of environmental Pu analysis, and for instrument calibration using these materials. There is a strong need for matrix matched isotopic standards for use as quality control materials [32]. Especially in mass spectrometric analyses, where the reproducibility on Pu isotope ratio measurements is found to be excellent, the pedigree of the materials used as standards has large implications on the accuracy of the result. With modern mass spectrometers precision of $<0.01\%$ in the isotope ratio measurement is achievable for actinides [39–41]. Both accuracy and precision would have to be combined to appropriately estimate realistic uncertainties obtained in isotope ratio measurements [39–41]. Meanwhile, the certified Pu activity and statistical value of Pu isotopic ratio will also help in quickly establishing a suitable selection of RMs for Pu determination. Finally, we point out that the concurrent information on certified activity provided by RMs producer and statistical value of Pu isotopic ratio will also strengthen data quality in establishing a baseline for environmental Pu analysis and environmental risk assessment related to nuclear power plant operations that are seeing a dramatically rise in some countries.

Data sources and methods

Data sources

We collected over 600 data of Pu-RMs from more than 100 publications (the original data see in Supporting Information: spreadsheet S1), in which the matrices of the RMs included sediment/soil, seawater, biota and fallout. These Pu datasets were mainly extracted from data base websites such as the Web of Science, Google Scholar and Scopus when we input the keywords "plutonium and $^{240}Pu/^{239}Pu$ atom ratio" combined with the primary keyword "reference material and/or certified reference material". Data of Pu-RMs from geological and environmental reference materials (GeoReM) database are also included, which is download from http://georem.mpch-mainz.gwdg.de.

Data treatment

Assuming a non-parametric distribution of data for which distribution-free statistics are applicable, we recalculated the collected Pu data by statistical analyses. Each set of Pu data collected from the literature is assumed to have the same weight (i.e., weighted mean = arithmetic mean). The statistical values of Pu isotopic ratios were the arithmetic means with corresponding standard deviations when more than two results were reported or were weighted means with weighted uncertainties in the case of only two results being reported. The median values of Pu were calculated from all reported Pu results passing the following criterion of *Z*-score, rounded off to the most significant number of the uncertainty. Meanwhile, following the guidelines of the ISO [42] and NIST [43], we also calculated the expanded uncertainty with a coverage factor of $k = 1.96$, corresponding to a level of confidence of about 95%. Confidence intervals were taken from a non-parametric sample population representing a two-sided interval at 95% confidence limits.

Following the recommendations from the ISO [44] and International Union of Pure and Applied Chemistry (IUPAC) [45], we calculated the statistical value along with the application of an appropriate target standard deviation, namely, a *Z*-score as suggested by the following equation:

$$Z = \frac{X_i - X_a}{S_b} \tag{1}$$

where X_i is the reported Pu isotopic ratios or activities from the literature *i*, X_a is a mean value of combined results and S_b indicates the target standard deviation. In general, the relative bias in radioactive analysis is below 20% ($S_b < 10\%$). We included the uncertainty of the assigned value (S_{tu}) in the target value for bias [46].

$$Z = \frac{X_i - X_a}{\sqrt{S_{tu}^2 + S_b^2}} \tag{2}$$

The accuracy of the Pu isotopic ratio and the activity from different publications was expressed by the *Z*-score for each RM. We thought a result was acceptable when this relative difference between the average value and the assigned value was below or equal to 2, indicating about 95% of the data points were between a *Z*-score of −2 and +2. Otherwise, the acceptable result from the extreme of the distribution had about a 1 in 20 chance when the *Z*-score was outside $|Z| > 2$. Furthermore, the chance that the result was acceptable was only about 1 in 300 when the *Z*-score was outside $|Z| > 3$ [47]. In addition, the median absolute deviation (MAD) is a measure of statistical dispersion, which is in detail described in elsewhere [48]. In brief, assuming the data follows the Gaussian distribution, the outliers fall in 50% of the area on both sides and the normal values fall in 50% of the area in the middle [48]. The MAD is simultaneously used to test statistical dispersion and to get rid of the outliers in a data set in this study. The results show that the two methods are consistent, which is potentially due to the results of the same RM measured in each laboratory are relatively concentrated and they have no big deviation.

Results and discussion

We summarized 30 RMs for the environmental Pu analysis, thoroughly covering the matrices of sediment/soil, seawater, biota and fallout. We tested the performance of the Pu dataset for each RM through the *Z*-score distribution. Here, taking IAEA-135 and IAEA-368 as typical examples, we discuss in detail their *Z*-score distributions for $^{239+240}Pu$ activity and $^{240}Pu/^{239}Pu$ atom ratio. As shown in Fig. 1, the *Z*-scores of $^{239+240}Pu$ activity and $^{240}Pu/^{239}Pu$ atom ratio for IAEA-135 and IAEA-368 were between −2 and +2, and that indicated the Pu datasets from different publications were satisfactory. We excluded the data point if the *Z*-score outliers $|Z| > 2$ and recalculated until a satisfactory result was obtained. Finally, we calculated the statistical values for each RM and tabulated them (Table 1).

Pu-RMs in sediment and soil

Activity level of Pu

The evaluation results in order of ascending activities, the distribution of medians and corresponding standard deviation for four typical RMs (IAEA-135, IAEA-368, IAEA-384 and NIST-4357) are shown in Fig. 2.

IAEA-135 (Irish Sea Sediment): the $^{239+240}Pu$ activities showed a consistent result although they were sourced from the determination results of different instruments. For example, the $^{239+240}Pu$ activity measured by ICP-MS ranged from 222 to 238 Bq kg^{-1} (average = 224 ± 10 Bq kg^{-1}) [49] and that analyzed by semiconductor alpha-spectrometry (SAS) was in the range of 216–228 Bq kg^{-1} (average = 222 ± 7 Bq kg^{-1}) [49]. The $^{239+240}Pu$ concentration determined by AMS was also in good agreement with the values of ICP-MS and SAS, being 221 ± 16 Bq kg^{-1} [49]. Through analyzing the published $^{239+240}Pu$ activity of IAEA-135 [31, 49–63], we found these Pu data showed good homogeneity, falling less than two standard deviations from the distribution mean (Fig. 2a). The statistical value of $^{239+240}Pu$ activities for IAEA-135 was 218.2 ± 6.8 Bq kg^{-1} (*n* = 25,

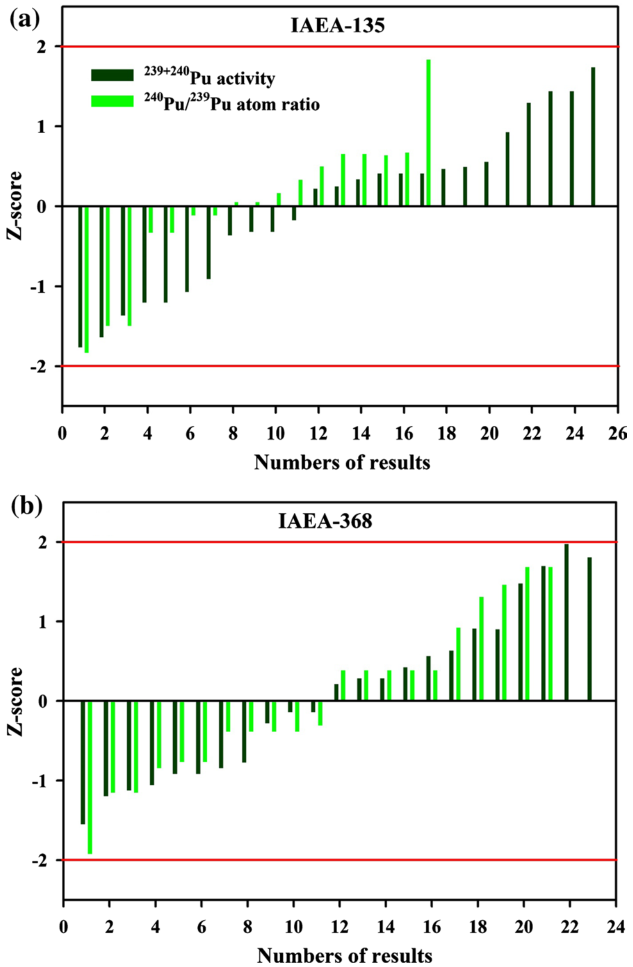

Fig. 1 Distributions of *Z*-scores of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio for IAEA-135 (**a**) and IAEA-368 (**b**)

the 95% confidence interval is 215.9–220.5 Bq kg^{-1}). This statistical value was comparable to those certified by IAEA (205–226 Bq kg^{-1}), indicating these measured values are highly reliable. The median given as the statistical value is 219.9 Bq kg^{-1}. Meanwhile, the statistical values of ^{238}Pu and ^{241}Pu activities were 34.6 ± 1.7 Bq kg^{-1} ($n = 12$) and 890 ± 141 Bq kg^{-1} ($n = 14$) (corrected to January 1, 2020 for the convenience of reference and comparison in the future study), respectively. The 95% confidence level interval corresponds to be 33.8–35.4 Bq kg^{-1} and 828–952 Bq kg^{-1}.

IAEA-368 (Ocean Sediment-Mururoa Atoll): the $^{239+240}$Pu dataset was evaluated using more than ten international reports [17, 28, 31, 51, 55, 57, 58, 64–76], and they showed good homogeneity as suggested by the *Z*-scores (all below 2). As shown in Fig. 2b, the reported $^{239+240}$Pu activities had a narrow range, falling within two standard deviations from the distribution mean. Our given statistical value of $^{239+240}$Pu activities was 31.2 ± 1.4 Bq kg^{-1} ($n = 22$, the 95% confidence interval is 30.7–31.7 Bq kg^{-1}). This statistical value is highly consistent with those certified by IAEA (29–34 Bq kg^{-1}), indicating these measured values are highly reliable. The median given as the statistical value is 31.3 Bq kg^{-1}. The statistical value of ^{238}Pu and ^{241}Pu activity was 7.0 ± 0.4 Bq kg^{-1} ($n = 2$) and 4.21 ± 0.38 Bq kg^{-1} ($n = 4$) (the 95% confidence level interval corresponds to be 6.6–7.4 Bq kg^{-1} and 3.90–4.52 Bq kg^{-1}), respectively.

IAEA-384 (Fangataufa Lagoon Sediment): the combined $^{239+240}$Pu dataset from different international laboratories showed good homogeneity as the *Z*-scores were less than 2 [12, 13, 31, 35, 37, 49, 53, 67, 76–84]. The reported Pu activity had a narrow range, falling within two standard deviations from the distribution mean (Fig. 2c). Our statistical value of $^{239+240}$Pu activities was 108.4 ± 2.7 Bq kg^{-1} ($n = 19$, the 95% confidence interval is 107.0–109.8 Bq kg^{-1}). This statistical value is highly consistent with those certified by IAEA (103–110 Bq kg^{-1}). The median given as the statistical value is 108.7 Bq kg^{-1}. Meanwhile, we recommended the statistical values of ^{238}Pu and ^{241}Pu activities to be 33.8 ± 1.7 Bq kg^{-1} ($n = 8$) and 21.5 ± 1.9 Bq kg^{-1} ($n = 7$) (the 95% confidence level interval corresponds to be 32.8–34.8 Bq kg^{-1} and 20.3–22.7 Bq kg^{-1}), respectively.

NIST-4357 (Ocean Sediment): the $^{239+240}$Pu data representing means obtained by different international laboratories were used in the calculation process [17, 50, 61, 70, 73, 74, 85–91]. These Pu data fell within less than two standard deviations from the distribution mean (Fig. 2d). The *Z*-scores were also between − 2 and + 2, showing good consistency in the Pu dataset. The statistical value of $^{239+240}$Pu activity was 9.96 ± 0.47 Bq kg^{-1} ($n = 13$, the 95% confidence interval is 9.74–10.18 Bq kg^{-1}). This statistical value is highly consistent with the certified values from IAEA (9.2–13.3 Bq kg^{-1}), indicating these measured values are highly reliable. The median given as the statistical value is 9.90 Bq kg^{-1}. Meanwhile, the statistical value of ^{238}Pu and ^{241}Pu activity was 1.93 ± 0.01 Bq kg^{-1} ($n = 2$) and 45.0 ± 2.6 Bq kg^{-1} ($n = 4$) (the 95% confidence level interval corresponds to be 1.92–1.94 Bq kg^{-1} and 42.9–47.1 Bq kg^{-1}), respectively.

Using the above method, we also analyzed 18 other Pu-RMs, namely, IAEA-300, IAEA-306, IAEA-307, IAEA-315, IAEA-326, IAEA-327, IAEA-367, IAEA-375, IAEA-385, IAEA-410, IAEA-412, IAEA-447, IAEA-soil-6, NIST-1646a, NIST-2702, NIST-4350b, NIST-4353 and NIST-4354. The statistical values of $^{238-241}$Pu activities are presented in Table 1, which were comparable to their certified values. The Pu isotopic ratios of RMs are usually not certified by the approving agency such as the IAEA and NIST. However, these isotopic ratios of Pu are very important to trace Pu sources and calibrate measurement methods. Therefore, we further analyzed isotopic ratios of Pu-RMs and reported their statistical values.

Table 1 Activity levels and isotopic ratios of Pu-RMs

Reference material	^{238}Pu activity (Bq kg^{-1})	$^{239+240}$Pu activity (Bq kg^{-1})	^{241}Pu activity (Bq kg^{-1})	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
Sediment/soil							
IAEA-135(Irish sea sediment)							
Statistical values (SV)[a]							
Mean ± SD	34.6 ± 1.7 (n=12)[c]	218.2 ± 6.8 (n=25)	890 ± 141 (n=14)	0.153 ± 0.008 (n=5)	0.209 ± 0.008 (n=18)	0.0047 ± 0.0007 (n=7)	[31, 49–63, 92–98, 121–124]
95% conf. int.[b]	33.8–35.4	215.9–220.5	828–952	0.147–0.159	0.206–0.212	0.0043–0.0051	
Median	34.5	219.9	885	0.152	0.210	0.0045	
Certified (information) values (95% conf. int.)	34.5 (33.3–36.1)	213 (205–225.8)	–	–	–	–	IAEA Certificate-135[d]
IAEA-300 (Baltic sea sediment)							
SV							
Mean ± SD	0.141 ± 0.018 (n=3)	3.50 ± 0.07 (n=8)	4.04 ±0.60 (n=1)	0.041 ± 0.005 (n=1)	0.185 ± 0.009 (n=6)	–	[55, 60, 61, 67, 86, 95, 104, 125–130]
95% conf. int.	0.123–0.159	3.46–3.54	–	–	0.179–0.191	–	
Median	0.132	3.49	–	–	0.189	–	
Certified values	–	3.43 (3.09–3.90)	–	–	–	–	IAEA Certificate-300
IAEA-306 (Baltic sea sediment)							
SV							
Mean ± SD	–	5.90 ± 0.14 (n=2)	–	–	0.166 ± 0.010 (n=1)	–	[31, 131]
95% conf. int.	–	5.73–6.07	–	–	–	–	
Median	–	5.90	–	–	–	–	
Certified values	–	5.7 (5.5–6.3)	–	–	–	–	IAEA Certificate-306
IAEA-307 (Mediterranean sea sediment)							
SV							
Mean ± SD	0.019 (n=1)	0.69 ± 0.05 (n=2)	–	–	0.219 ± 0.016 (n=1)	–	[31, 132]
95% conf. int.	–	0.63–0.75	–	–	–	–	
Median	–	0.69	–	–	–	–	
Certified values	–	0.71 (0.45–0.97)	–	–	–	–	IAEA Certificate-307
IAEA-315 (Marine sediment)							
SV							
Mean ± SD	8.6 ± 0.4 (n=1)	66.3 ± 1.5 (n=3)	–	0.1303 ± 0.0096(n=1)	0.208 ± 0.003 (n=1)	0.0068 ± 0.0002 (n=1)	[133]
95% conf. int.	–	64.8–67.8	–	–	–	–	
Median	–	66.0	–	–	–	–	
Certified values	–	–	–	–	–	–	–
IAEA-326 (Kursk/Russia soil)							
SV							
Mean ± SD	0.0164 ± 0.0017 (n=3)	0.492 ± 0.046 (n=6)	1.2 ± 0.3 (n=1)	0.032 ± 0.008 (n=2)	0.185 ± 0.009 (n=3)	–	[61, 69, 76, 96, 134, 135]
95% conf. int.	0.0148–0.0180	0.461–0.523	–	0.023–0.041	0.176–0.194	–	
Median	0.0164	0.500	–	0.032	0.180	–	
Reference values	0.0140–0.0172	0.48–0.52	–	–	–	–	IAEA Certificate-326
IAEA-327							
SV							
Mean ± SD	0.018 ± 0.001 (n=4)	0.585 ± 0.020 (n=6)	0.66 ± 0.21 (n=1)	0.030 ± 0.003 (n=2)	0.189 ± 0.008 (n=4)	–	[60, 61, 76, 96, 134, 136, 137]
95% conf. int.	0.017–0.019	0.572–0.598	–	0.027–0.033	0.182–0.196	–	
Median	0.018	0.589	–	0.030	0.191	–	

Table 1 (continued)

Reference material	^{238}Pu activity (Bq kg^{-1})	$^{239+240}$Pu activity (Bq kg^{-1})	^{241}Pu activity (Bq kg^{-1})	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
Reference values	0.015–0.018	0.56–0.60	–	–	–	–	IAEA Certificate-327
IAEA-367 (Enewetak atoll sediment)							
SV							
Mean ± SD	0.063 (n = 1)	36.82 ± 1.13 (n = 10)	39.1 ± 1.4 (n = 3)	–	0.297 ± 0.002 (n = 12)	0.00149 ± 0.00009 (n = 3)	[31, 37, 67, 76, 81, 82, 86, 92, 93, 138–141]
95% conf. int.	–	36.23–37.41	37.8–40.4	–	0.296–0.298	0.00141–0.00157	
Median	–	36.86	39.6	–	0.297	0.00147	
Certified values	–	38 (34.4–39.8)	–	–	–	–	IAEA Certificate-367
IAEA-368 (Mururoa atoll sediment)							
SV							
Mean ± SD	7.0 ± 0.4 (n = 2)	31.2 ± 1.4 (n = 22)	4.21 ± 0.38 (n = 4)	0.232 ± 0.047 (n = 1)	0.0326 ± 0.0013 (n = 20)	0.000170 ± 0.000121 (n = 7)	[17, 28, 31, 51, 55, 57, 58, 64–76, 86, 92, 97, 98, 100, 101, 142]
95% conf. int.	6.6–7.4	30.7–31.7	3.90–4.52	–	0.0321–0.0331	0.000095–0.000245	
Median	7.0	31.3	4.09	–	0.0326	0.000125	
Certified values	–	31 (29–34)	–	–	–	–	IAEA Certificate-368
IAEA-375 (Chernobyl soil)							
SV							
Mean ± SD	0.056 ± 0.005 (n = 7)	0.290 ± 0.034 (n = 21)	1.56 ± 0.39 (n = 1)	0.173 ± 0.020 (n = 2)	0.278 ± 0.048 (n = 9)	–	[55, 60–62, 64, 67, 69, 75, 76, 84, 93, 109, 127, 137, 143–148]
95%conf. int.	0.053-0.059	0.278–0.302	–	0.150–0.196	0.252–0.304	–	
Median	0.053	0.294	–	0.173	0.296	–	
Information values	0.057 (0.045–0.068)	0.30 (0.26–0.34)	–	–	–	–	IAEA Certificate-375
IAEA-384 (Fangataufa Lagoon sediment)							
SV							
Mean ± SD	33.8 ± 1.7 (n = 8)	108.4 ± 2.7 (n = 19)	21.5 ± 1.9 (n = 7)	0.310 ± 0.009 (n = 5)	0.051 ± 0.001 (n = 13)	0.00017 ± 0.00002 (n = 1)	[12, 13, 31, 35, 37, 49, 53, 67, 76–84, 100, 102, 123, 149]
95%conf. int.	32.8–34.8	107.0–109.8	20.3–22.7	0.303–0.317	0.050–0.052	–	
Median	34.1	108.7	21.6	0.307	0.050	–	
Certified	35.2 (34.8–35.7)	107 (103–110)	–	–	–	–	IAEA Certificate-384
IAEA-385 (Irish sea sediment)							
SV							
Mean ± SD	0.411 ± 0.068 (n = 4)	2.90 ± 0.12 (n = 17)	9.7 ± 1.9 (n = 4)	0.127 ± 0.009 (n = 1)	0.184 ± 0.008 (n = 8)	0.00317 ± 0.00028 (n = 1)	[12, 13, 31, 38, 78, 79, 82, 87, 91, 123, 150–153]
95%conf. int.	0.355–0467	2.85–2.95	8.1–11.3	–	0.179–0.189	–	
Median	0.380	2.94	9.2	–	0.185	–	
Certified (information) values	0.40 (0.38–0.43)	2.96 (2.89–3.00)	9.5 (8.2–10.1) (inf. val.)	–		–	IAEA Certificate385
IAEA-410 (Bikini atoll sediment)							
SV							
	0.068 ± 0.019 (n = 1)	4.68 ± 0.48 (n = 1)	–	0.015 ± 0.004 (n = 1)		–	[154]
Certified (information) values	0.068 (0.050–0.086) (inf. val.)	4.68 (4.2–5.2)	–	–	–	–	IAEA Certificate-410
IAEA-412 (Pacific Ocean sediment)							
SV							
	0.0188 ± 0.0038 (n = 1)	0.596 ± 0.022 (n = 2)	–	0.031 ± 0.007 (n = 1)	–	–	[153, 154]

Table 1 (continued)

Reference material	^{238}Pu activity (Bq kg^{-1})	$^{239+240}$Pu activity (Bq kg^{-1})	^{241}Pu activity (Bq kg^{-1})	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
Certified (information) values	0.0188 (0.0015–0.0226) (inf. val.)	0.611 (0.58–0.64)	–	–	–	–	IAEA Certificate-412
IAEA-447 (Moss soil)							
SV							
Mean ± SD	0.138 ± 0.014 (n = 1)	5.22 ± 0.21 (n = 4)	4.92 ± 0.62 (n = 1)	0.026 ± 0.003 (n = 1)	0.18 ± 0.01 (n = 1)	–	[76, 155–157]
95%conf. int.	–	5.04–5.40	–	–	–	–	
Median	–	5.32	–	–	–	–	
Certified values	0.138 (0.120–0.156)	5.3 (5.14–5.46)	4.94 (4.22–5.56) (inf. val.)	–	–	–	IAEA Certificate-447
IAEA-Soil-6 (Austrian soil)							
SV							
Mean ± SD	0.023 ± 0.005 (n = 3)	1.016 ± 0.027 (n = 20)	1.14 ± 0.20 (n = 3)	0.021 ± 0.004 (n = 3)	0.191 ± 0.003 (n = 11)	0.0075 ± 0.0008 (n = 1)	[17, 51, 55, 57, 61, 65, 67, 74, 84, 86, 93, 97, 109, 129, 141, 147, 148, 158–163]
95%conf. int.	0.018–0.028	1.006–1.026	0.95–1.33	0.017–0.025	0.189–0.193	–	
Median	0.025	1.008	1.16	0.023	0.191	–	
Certified values	–	1.04 (0.96–1.11)	–	–	–	–	IAEA Certificate-Soil 6
NIST-1646a							
SV	–	0.204 ± 0.006 (n = 2)	–	–	0.173 ± 0.003 (n = 2)	–	[90, 91]
Certified values	–	–	–	–	–	–	–
NIST-2702							
SV	–	0.363 ± 0.021 (n = 2)	–	–	0.178 ± 0.009 (n = 2)	–	[90, 91]
Certified values	–	–	–	–	–	–	–
NIST-4350b (Columbia river sediment)							
SV							
Mean ± SD	–	0.530 ± 0.033 (n = 4)	–	–	0.112 ± 0.009 (n = 3)	–	[55, 87, 133, 164]
95%conf. int.	–	0.503–0.557	–	–	0.103–0.121	–	
Median		0.537	–	–	0.117	–	
Certified values	0.096 (0.080–0.112)	0.508 (0.48–0.54)	–	–	–	–	NIST Certificate-4350b
NIST-4353 (Rocky flats soil)							
SV							
Mean ± SD	–	8.68 ± 1.00 (n = 3)	–	–	0.060 ± 0.002 (n = 2)	–	[50, 87, 89]
95%conf. int.	–	7.73–9.63	–	–	0.058–0.062	–	
Median	–	8.30	–	–	0.060	–	
Certified values	–	8.10 (7.37–8.63)	–	–	–	–	NIST Certificate-4353
NIST-4354 (Freshwater lake sediment)							
SV							
Mean ± SD	–	3.94 ± 0.12 (n = 5)	–	–	0.162 ± 0.018 (n = 7)	0.0019 ± 0.0008 (n = 1)	[61, 65, 68, 72, 97, 101, 133, 145, 165]
95%conf. int.	–	3.85–4.03	–	–	0.151–0.173	–	
Median	–	3.94	–	–	0.153	–	
Certified values	0.199 (0.180–0.218)	4.0 (3.28–4.16)	–	–	–	–	NIST Certificate-4354

Table 1 (continued)

Reference material	^{238}Pu activity (Bq kg^{-1})	$^{239+240}$Pu activity (Bq kg^{-1})	^{241}Pu activity (Bq kg^{-1})	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
NIST-4357 (Ocean sediment)							
SV							
Mean ± SD	1.93 ± 0.01 (n = 2)	9.96 ± 0.47 (n = 13)	45.0 ± 2.6 (n = 4)	0.192 ± 0.010 (n = 2)	0.233 ± 0.004 (n = 10)	0.00507 ± 0.00008 (n = 3)	[17, 50, 61, 70, 73, 74, 85–91]
95%conf. int.	1.92–1.94	9.74–10.18	42.9–47.1	0.180–0.204	0.231–0.235	0.00499–0.00515	
Median	1.93	9.90	44.4	0.192	0.233	0.00504	
Certified values	1.93 (1.80–1.98)	10.4 (9.2–13.3)	–	–	–	–	NIST Certificate-4357

Certified Reference material	^{238}Pu activity (mBq kg^{-1})	$^{239+240}$Pu activity (mBq kg^{-1})	^{241}Pu activity (mBq kg^{-1})	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
Liquid (seawater/water)							
IAEA-381 (Irish sea water)							
SV							
Mean ± SD	2.61 ± 0.12 (n = 6)	14.7 ± 0.7 (n = 12)	83.3 ± 7.0 (n = 3)	0.182 ± 0.002 (n = 3)	0.236 ± 0.005 (n = 8)	–	[49, 86, 104–112, 116, 123, 166, 167]
95%conf. int.	2.53–2.69	14.4–15.0	78.1–88.5	0.181–0.183	0.233–0.239	–	
Median	2.61	14.8	79.4	0.182	0.238	–	
Certified values	2.86 (2.80–3.16)	14.2 (13.2–15.2)	–	–	–	–	IAEA Certificate-381
IAEA-443 (Irish sea water)							
SV							
Mean ± SD	2.80 ± 0.09 (n = 1)	15.2 ± 0.7 (n = 7)	95.9 ± 13.3 (n = 4)	0.192 ± 0.008 (n = 1)	0.232 ± 0.003 (n = 7)	–	[12, 13, 27, 111–115, 117, 118, 168]
95%conf. int.	–	14.7–15.7	84.9–106.9	–	0.230–0.234	–	
Median	–	14.7	94.1	–	0.233	–	
Certified (information) values	2.80 (2.60–2.90)	14.7 (14.3–15.0)	86 (75–97) (inf. val.)	–	–	–	IAEA Certificate-443
CRM-NBL-122							
SV	–	–	–	–	0.1321 ± 0.0001 (n = 1)	–	[169]
Certified values	–	–	–	–	0.1320	–	NBL Certificate-122
CRM-NBL-126							
SV	–	–	–	–	0.0204 (n = 1)	–	[169]
Certified values	–	–	–	–	0.0209	–	Certificate-126
CRM-NBL-128							
SV	–	–	–	–	0.0007 (n = 1)	–	[169]
Certified values	–	–	–	–	0.0007	–	NBL Certificate-128
CRM-NBL-137							
SV	–	–	–	–	0.2432 ± 0.0015 (n = 1)	0.00590 ± 0.00012 (n = 1)	[59]
Certified values	–	–	–	–	0.2410	0.00574	NBL Certificate-137

Certified Reference material	^{238}Pu activity (Bq kg^{-1} d.w.)	$^{239+240}$Pu activity (Bq kg^{-1} d.w.)	^{241}Pu activity (Bq kg^{-1} d.w.)	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
Biota							
IAEA-134 (Fish flesh from the Irish sea)							
SV							
Mean ± SD	2.53 ± 0.18 (n = 2)	15.6 ± 0.9 (n = 5)	59.8 ± 5.2 (n = 1)	0.153 ± 0.008 (n = 2)	0.208 ± 0.005 (n = 4)	–	[31, 49–51, 92]
95%conf. int.	2.32–2.74	14.9–16.3	–	0.144–0.162	0.203–0.213	–	
Median	2.53	15.4	–	0.153	0.210	–	

Table 1 (continued)

Certified Reference material	^{238}Pu activity (Bq kg^{-1} d.w.)	$^{239+240}$Pu activity (Bq kg^{-1} d.w.)	^{241}Pu activity (Bq kg^{-1} d.w.)	^{238}Pu/$^{239+240}$Pu activity ratio	^{240}Pu/^{239}Pu atom ratio	^{241}Pu/^{239}Pu atom ratio	Literature
Certified (reference) values	2.52–2.86 (reference values)	15 (13.8–16.2)	–	–	–	–	IAEA Certificate-134
IAEA-414 (Mixed fish flesh from the Irish sea and north sea)							
SV							
Mean ± SD	0.0193 ± 0.0009 (n=5)	0.120 ± 0.008 (n=7)	0.607 ± 0.123 (n = 2)	0.164 ± 0.006 (n=3)	0.208 ± 0.018 (n=1)	0.0064 ± 0.0012 (n=1)	[78, 80, 84, 123, 154, 170, 171]
95%conf. int.	0.0186–0.0200	0.115–0.125	0.463–0.751	0.158–0.170	–	–	
Median	0.0192	0.120	0.607	0.162	–	–	
Certified (reference) values	0.0191 (0.0184–0.0208)	0.120 (0.116–0.123)	0.66 (0.60–0.76) (ref. val.)	–	–	–	IAEA Certificate-414
IAEA-446 (Baltic sea seaweed)							
SV	–	0.024 ± 0.002 (n=1)	–	–	0.222 ± 0.047 (n=1)	–	[172]
Certified value	–	0.024 (0.022–0.026)	–	–	–	–	IAEA Certificate-446
Reference material	**^{238}Pu activity (Bq kg^{-1} d.w.)**	**$^{239+240}$Pu activity (Bq kg^{-1} d.w.)**	**^{241}Pu activity (Bq kg^{-1} d.w.)**	**^{238}Pu/$^{239+240}$Pu activity ratio**	**^{240}Pu/^{239}Pu atom ratio**	**^{241}Pu/^{239}Pu atom ratio**	**Literature**
Fallout							
Japanese fallout in 1963–1979							
SV	–	6.68 ± 0.16 (n=1)	4.74 ± 0.16 (n=1)	–	0.191 ± 0.001 (n=2)	0.00104 ± 0.00021 (n=1)	[70, 101]
Reference values	0.218 ± 0.089 (n=1)	6.61 ± 0.42 (n=1)	–	0.033 ± 0.012 (n=1)	–	–	[120]

[a]We calculated the values from the literature as statistical value (SV) in this study. [b]The certified (information/reference) values were from the approving agency (e.g., IAEA and NIST) and data in parentheses indicate the confidence interval of 95%. [c]n indicates the number of measured values in different method from the literatures. [d]The IAEA and NIST certificates are available from https://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Radionuclides/index.htm and https://www-s.nist.gov/srmors/browseMaterials.cfm?subkey=19&tableid=131

Reference date for reporting the Pu data ($^{238-241}$Pu): January 1, 2020. "–" indicates no data

Isotopic ratio of Pu

The evaluation results in order of ^{240}Pu/^{239}Pu atom ratio, the distribution of medians and corresponding standard deviation for four typical RMs (namely, IAEA-135, IAEA-368, IAEA-384 and NIST-4357) are presented in Fig. 3.

IAEA-135 (Irish Sea Sediment): the ^{240}Pu/^{239}Pu atom ratio showed a consistent result although they were sourced from the determination results of different instruments. For example, the ^{240}Pu/^{239}Pu atom ratio measured by ICP-MS was 0.207 ± 0.006, which was consistent with the AMS result (0.219 ± 0.022) [49]. As shown in Fig. 3a, the ^{240}Pu/^{239}Pu atom ratio showed good homogeneity, falling less than two standard deviations from the distribution mean. After analyzing the published ^{240}Pu/^{239}Pu atom ratios [31, 49, 51, 54, 58, 61, 92–98], we recommended the statistical value of the ^{240}Pu/^{239}Pu atom ratio for IAEA-135 to be 0.209 ± 0.008 (n = 18, the 95% confidence interval is 0.206–0.212), with the variation of ^{240}Pu/^{239}Pu atom ratio below 4%. The median given as the statistical value is 0.210. Such a statistical value was higher than that of global fallout [18] because low-level liquid radioactive waste from BNFL Sellafield was discharged to the Irish Sea from 1952 to 1992 [99]. Meanwhile, the statistical values of ^{238}Pu/$^{239+240}$Pu activity ratios and ^{241}Pu/^{239}Pu atom ratios were recommended to be 0.153 ± 0.008 (n = 5) and 0.0047 ± 0.0007 (n = 7) (the 95% confidence level interval corresponds to be 0.147–0.159 and 0.0043–0.0051), respectively.

IAEA-368 (Ocean Sediment-Mururoa Atoll): we evaluated the ^{240}Pu/^{239}Pu atom ratios using findings from more than ten international laboratories [17, 28, 31, 51, 58, 64, 65, 68, 70–75, 86, 92, 97, 98, 100, 101]. The ^{240}Pu/^{239}Pu atom ratios showed good homogeneity because the Z-scores were below 2. As shown in Fig. 3b, the ^{240}Pu/^{239}Pu atom ratios fell within two standard deviations from the distribution mean. The statistical value of the ^{240}Pu/^{239}Pu atom ratios for IAEA-368 was reported to be 0.0326 ± 0.0013 (n = 20, the 95% confidence interval is 0.0321–0.0331), which was comparable to that obtained in weapons-grade Pu [20] and was significantly lower than that of global fallout [18]. The median given as the statistical value is 0.0326. Meanwhile, the ^{238}Pu/$^{239+240}$Pu activity ratios and ^{241}Pu/^{239}Pu atom ratios

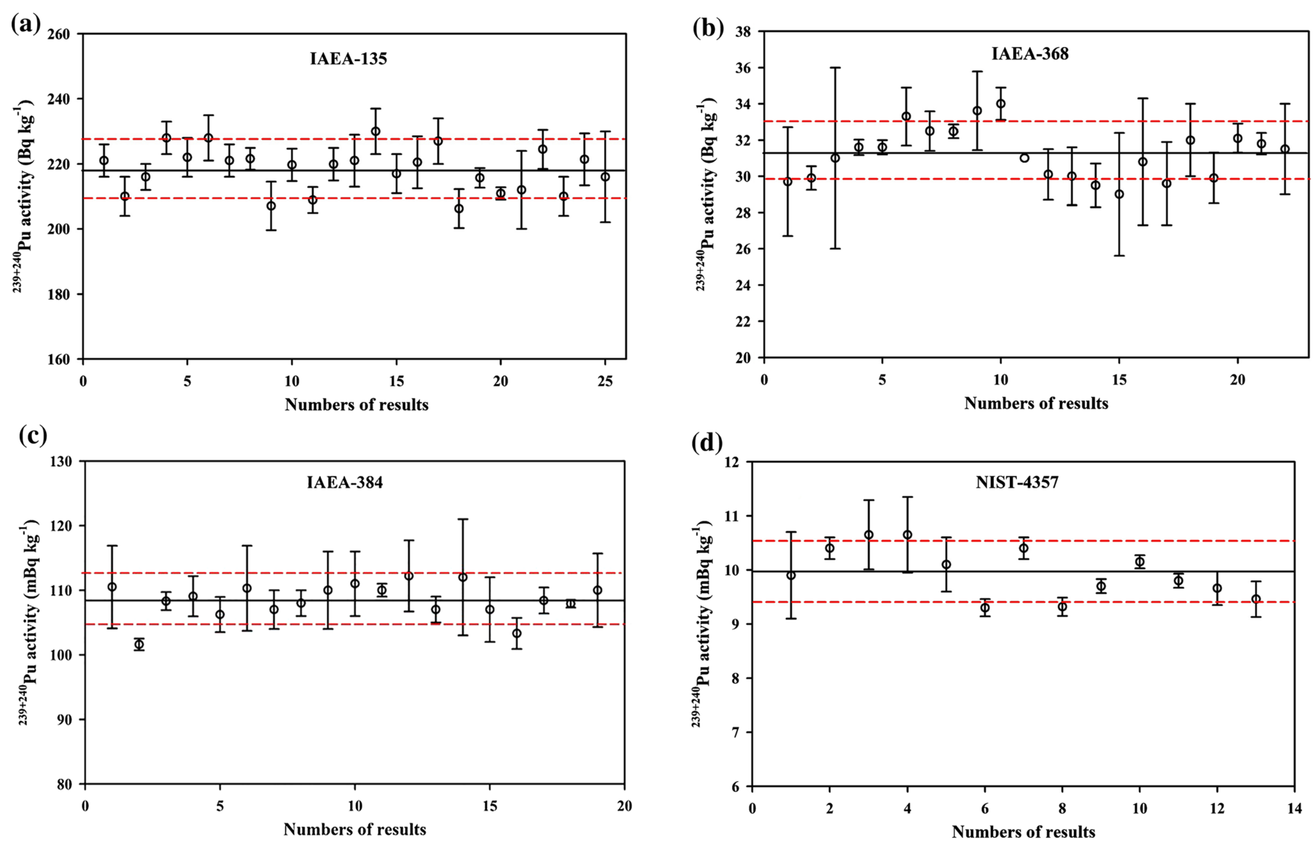

Fig. 2 Data evaluation for $^{239+240}$Pu activity in IAEA-135 (**a**), IAEA-368 (**b**), IAEA-384 (**c**) and NIST-4357 (**d**). The median (black solid line) and corresponding standard deviation (red dashed lines) are shown. The error bars correspond to the combined uncertainty reported in the literature. (Color figure online)

were recommended to be 0.232 ± 0.047 (n = 1) and 0.000170 ± 0.000121 (n = 7), respectively.

IAEA-384 (Fangataufa Lagoon Sediment): we summarized the published ^{240}Pu/^{239}Pu atom ratios from the literature [12, 13, 31, 35, 37, 49, 76, 81, 82, 102], and they showed good homogeneity as the Z-scores were below 2. As shown in Fig. 3c, the ^{240}Pu/^{239}Pu atom ratios had a narrow range, falling within two standard deviations from the distribution mean. Our statistical value of ^{240}Pu/^{239}Pu atom ratio for IAEA-384 was 0.051 ± 0.001 (n = 13, the 95% confidence interval is 0.050–0.052), with the variation of ^{240}Pu/^{239}Pu atom ratio below 2%. The median given as the statistical value is 0.050. Such a statistical value was comparable to that obtained in weapons-grade Pu [20] and was reasonable considering the 193 French nuclear weapon tests (equivalent to 13.2 Mt TNT) conducted in the Mururoa and Fangataufa Atolls [103] resulted in ^{239}Pu enrichment of IAEA-384. The statistical value of ^{238}Pu/$^{239+240}$Pu activity ratios was 0.310 ± 0.009 (n = 5) (the 95% confidence interval is 0.303–0.317).

NIST-4357 (Ocean Sediment): we collected means from different international laboratories concerning the ^{240}Pu/^{239}Pu atom ratios for our calculation [17, 61, 70, 73, 74, 86–91]. The ^{240}Pu/^{239}Pu atom ratios fell within less than two standard deviations from the distribution mean (Fig. 3d). The Z-scores were also between − 2 and + 2, showing good consistency in the ^{240}Pu/^{239}Pu atom ratios. Our statistical value of ^{240}Pu/^{239}Pu atom ratios for NIST-4357 was 0.233 ± 0.004 (n = 10, the 95% confidence interval is 0.231–0.235), with the variation of ^{240}Pu/^{239}Pu atom ratio below 2%. The median given as the statistical value is 0.233. The statistical values of ^{238}Pu/$^{239+240}$Pu activity ratios and ^{241}Pu/^{239}Pu atom ratios were recommended to be 0.192 ± 0.010 (n = 2) and 0.00507 ± 0.00008 (n = 3) (the 95% confidence level interval corresponds to be 0.180–0.204 and 0.00499–0.00515), respectively.

Following the above method, the information values of Pu isotopic ratio from 18 other RMs (same as mentioned above) were also obtained and given in Table 1. Since the stocks of the existing primary standard are declining, the Pu standard with a certified isotopic ratio is not unable to meet the growing demands of Pu measurement. And the transport/import of Pu standard is a greater hurdle compared to the RMs. These statistical values of Pu isotopic ratios will thus help in calibrating the mass bias, by quickly establishing a suitable selection of RMs for Pu determination.

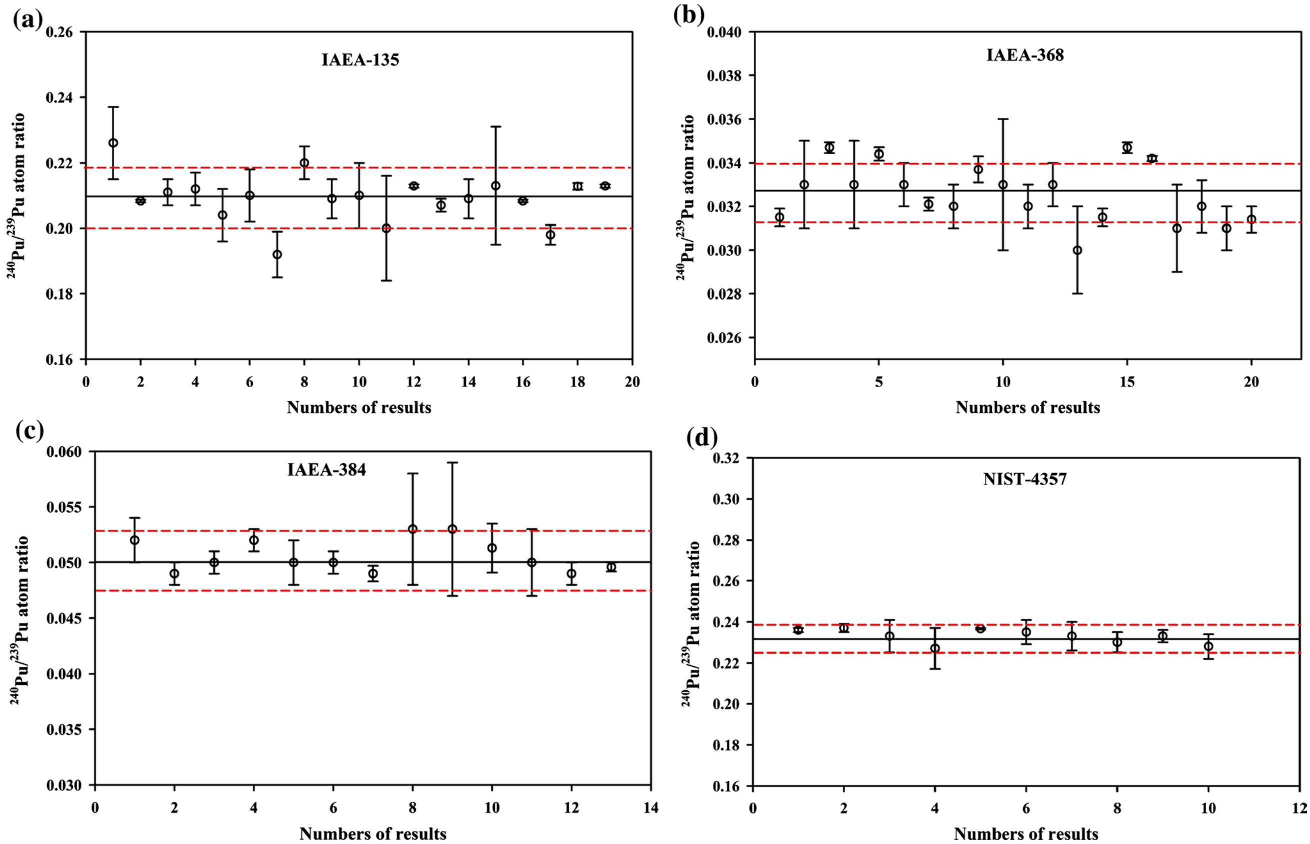

Fig. 3 Data evaluation for ^{240}Pu/^{239}Pu atom ratio in IAEA-135 (**a**), IAEA-368 (**b**), IAEA-384 (**c**) and NIST-4357 (**d**). The median (black solid line) and corresponding standard deviation (red dashed lines) are shown. The error bars correspond to the combined uncertainty reported in the literature. (Color figure online)

Pu-RMs in water

Activity levels of Pu

Two typical Pu-RMs in seawater, namely, IAEA-381 and IAEA-443, were analyzed using the *Z*-score and statistical evaluation.

IAEA-381 (Irish Sea Water): $^{239+240}$Pu activities used in our analyses were findings from multiple independent international laboratories [49, 104–112]. As shown in Fig. 4a, the *Z*-scores were less than 2, showing good consistency of the Pu dataset derived from findings of different laboratories. The $^{239+240}$Pu activities fell within less than two standard deviations from the distribution mean (Fig. 5a). The statistical value of $^{239+240}$Pu activities for IAEA-381 was calculated to be 14.7 ± 0.7 mBq kg^{-1} ($n = 9$, the 95% confidence interval is 14.4–15.0 mBq kg^{-1}). This statistical value is highly consistent with those certified by IAEA (13.2–15.2 mBq kg^{-1}), indicating these measured values are highly reliable. The median given as the statistical value is 14.8 Bq kg^{-1}. Meanwhile, the statistical values of ^{238}Pu and ^{241}Pu activities were calculated to be 2.61 ± 0.12 mBq kg^{-1} ($n = 6$) and 83.3 ± 7.0 mBq kg^{-1} ($n = 3$) (the 95% confidence level interval corresponds to be 2.53–2.69 mBq kg^{-1} and 78.1–88.5 mBq kg^{-1}), respectively.

IAEA-443 (Irish Sea Water): This RM has been recently provided by IAEA. We prepared our Pu dataset from the findings of multiple international laboratories [27, 111–115]. As shown in Fig. 4b, the *Z*-scores were below 2, showing good consistency of the Pu dataset from the findings of different laboratories. The $^{239+240}$Pu activities fell within less than two standard deviations from the distribution mean (Fig. 5c). Therefore, the statistical value of $^{239+240}$Pu activities for IAEA-443 was calculated to be 15.2 ± 0.7 mBq kg^{-1} ($n = 7$, the 95% confidence interval is 14.7–15.7 mBq kg^{-1}). This statistical value was comparable to those certified by IAEA (14.3–15.0 mBq kg^{-1}), indicating these measured values are highly reliable. The median given as the statistical value is 14.7 mBq kg^{-1}. Meanwhile, the statistical values of ^{238}Pu and ^{241}Pu activities were calculated to be 2.80 ± 0.09 mBq kg^{-1} ($n = 1$) and 95.9 ± 13.3 mBq kg^{-1} ($n = 4$), respectively.

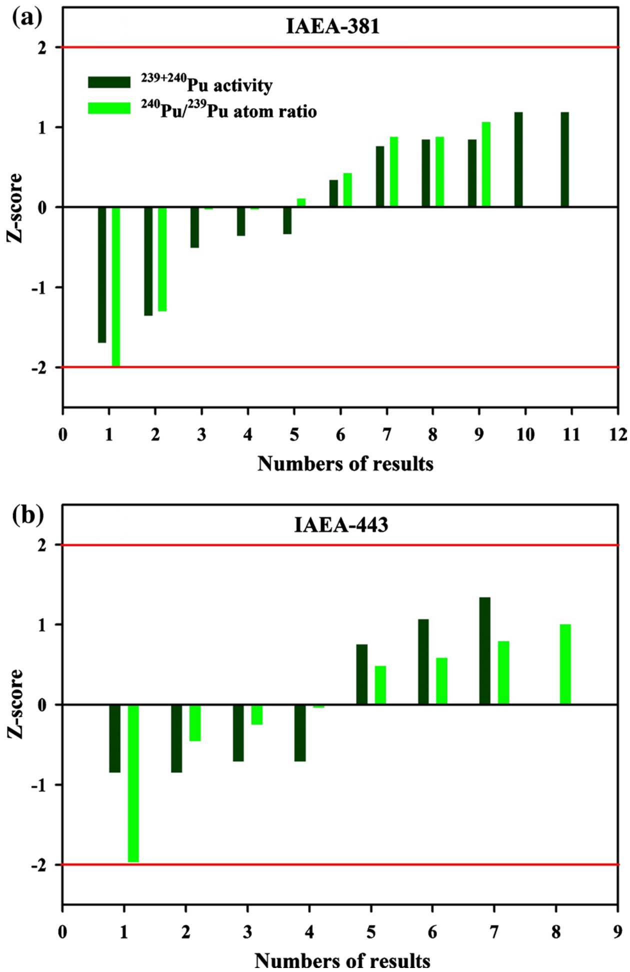

Fig. 4 Distributions of *Z*-scores of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio for IAEA-381 (**a**) and IAEA-443 (**b**)

Isotopic ratio of Pu

Information on isotopic ratio of Pu in the RMs was not certified by the IAEA. Here, we combined Pu isotopic data from the literature and derived their recommended values by statistical analyses.

IAEA-381 (Irish Sea Water): ^{240}Pu/^{239}Pu atom ratios of IAEA-381 have been extensively reported [49, 86, 104, 106, 108–110, 112, 116]. As shown in Fig. 4a, the *Z*-scores were below 2, showing good consistency of ^{240}Pu/^{239}Pu atom ratios provided by different laboratories. The ^{240}Pu/^{239}Pu atom ratios fell within less than two standard deviations from the distribution mean (Fig. 5b). The statistical value of ^{240}Pu/^{239}Pu atom ratios for IAEA-381 was calculated to be 0.236 ± 0.005 ($n=8$, the 95% confidence interval is 0.233–0.239), a variation in the results of ± 3.4%. The median given as the statistical value is 0.238. This statistical value was higher than that of global fallout because the radioactive waste from BNFL Sellafield was discharged to the Irish Sea from 1952 to 1992 [99]. In addition, the recommended value of ^{238}Pu/$^{239+240}$Pu activity ratios was calculated to be 0.182 ± 0.002 ($n=3$) (the 95% confidence interval is 0.181–0.183).

IAEA-443 (Irish Sea Water): We summarized the reported ^{240}Pu/^{239}Pu atom ratios from several international laboratories [12, 13, 111–113, 115, 117, 118]. As shown in Fig. 4b, the *Z*-scores were below 2, showing good consistency of ^{240}Pu/^{239}Pu atom ratios from different laboratories. The ^{240}Pu/^{239}Pu atom ratios fell within less than two standard deviations from the distribution mean (Fig. 5d). We recommended the statistical value of ^{240}Pu/^{239}Pu atom ratio for IAEA-443 to be 0.232 ± 0.003 ($n=7$, the 95% confidence interval is 0.230–0.234), a variation in the results of ± 1.3%. The median given as the statistical value is 0.233. This statistical value was comparable to those obtained for IAEA-381 and IAEA-135, which were also sampled from the Irish Sea. Meanwhile, the statistical value of ^{238}Pu/$^{239+240}$Pu activity ratio was recommended to be 0.192 ± 0.008 ($n=1$).

It is well known that the mass bias correction is necessary to obtain high quality data in the determination of Pu using ICP-MS [119]. However, the transport/import of Pu standard with a certified isotopic ratio presents the greatest hurdle at present for many laboratories working on environmental Pu analysis. Hence, calibration of the mass bias in the determination of Pu ratio by mass spectrometry is a difficult issue. In the absent of any Pu isotope ratio standard, the purification of Pu from high Pu concentration seawater obtained from the IAEA could be regarded as an alternative approach for the mass bias correction in the determination of Pu isotopic ratio considering the precision required for environmental Pu analysis. Of course, for safeguards analysis, which requires much higher precision for Pu isotope ratio analysis, certified Pu isotope ratio standards should be used, but this issue is beyond the scope of this study. Here, our statistical values of Pu isotopic ratios after the statistical analysis could be recommended to calibrate the mass bias (Table 1), which is very important for the validation of Pu measurement.

Pu-RMs in biota

We discussed in detail the RM in biota for IAEA-134 (sample matrix: fish flesh in Irish Sea) through combining the Pu data from literatures [31, 49–51, 92]. As shown in Fig. 6a, the *Z*-score values of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio were less than 2, showing good consistency of Pu dataset from the different laboratory. The $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios fell within less than two standard deviations from the distribution means (Fig. 6b, c). The statistical values of ^{238}Pu and $^{239+240}$Pu activities for IAEA-134 were calculated to be 2.53 ± 0.18 Bq kg^{-1} d.w. ($n=2$) and 15.6 ± 0.9 Bq kg^{-1}

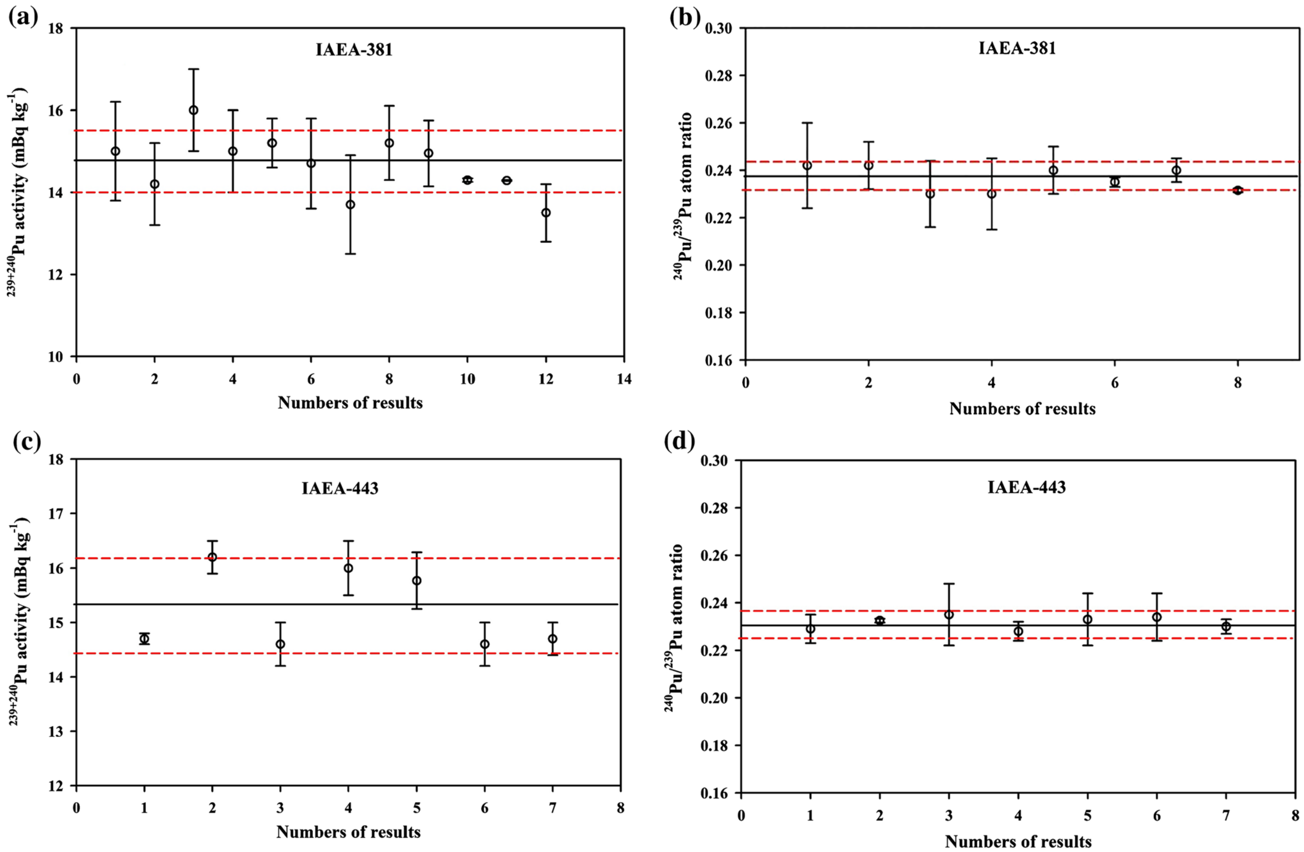

Fig. 5 Data evaluation for $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio in IAEA-381 (**a**, **b**) and IAEA-443 (**c**, **d**). The median (black solid line) and corresponding standard deviation (red dashed lines) are shown. The error bars correspond to the combined uncertainty reported in the literature. (Color figure online)

d.w. ($n=5$) (the 95% confidence level interval corresponds to be 2.32–2.74 Bq kg^{-1} d.w. and 14.9–16.3 Bq kg^{-1} d.w.), respectively. The statistical values of ^{238}Pu/$^{239+240}$Pu activity ratios and ^{240}Pu/^{239}Pu atom ratios were also calculated to be 0.153 ± 0.008 ($n=2$) and 0.208 ± 0.005 ($n=4$) (the 95% confidence level interval corresponds to be 0.144–0.162 and 0.203–0.213), respectively. The median given as the statistical value of ^{240}Pu/^{239}Pu atom ratio is 0.210. In addition, the statistical values of Pu activities and isotopic ratios for IAEA-414 (sample matrix: fish flesh) and IAEA-446 (sample matrix: seaweed) are also presented in Table 1.

Pu reference fallout material

Reference fallout material of Pu is very important for QC of fallout Pu analysis in atmospheric studies. However, scarcely any reference fallout material has been certified by NIST or IAEA. Otsuji-Hatori et al. [120] tried to prepare the reference fallout material using deposition samples collected at 14 Japanese meteorological stations during 1963–1979 and they measured the ^{238}Pu activities (0.218 ± 0.089 Bq kg^{-1} d.w.) and $^{239+240}$Pu activities (6.61 ± 0.42 Bq kg^{-1} d.w.) by α-spectrometry. The ^{238}Pu/$^{239+240}$Pu activity ratios were calculated to be 0.033 ± 0.012. Subsequently, Zhang et al. [70] measured the ^{241}Pu activities (4.62 ± 0.84 Bq kg^{-1} d.w.) and $^{239+240}$Pu activities (6.68 ± 0.16 Bq kg^{-1} d.w.) of reference fallout material in Japan using SF-ICP-MS. Their measured $^{239+240}$Pu activities were in good agreement with the reference value provided by Otsuji-Hatori et al. [120]. Meanwhile, the ^{240}Pu/^{239}Pu atom ratios and ^{241}Pu/^{239}Pu atom ratios were calculated to be 0.1919 ± 0.0005 and 0.00104 ± 0.00021, respectively. Recently, Ohtsuka et al. [101] measured the ^{240}Pu/^{239}Pu atom ratio of Japan fallout material to be 0.191 ± 0.003, which was in good agreement with Zhang et al.'s result [70]. Therefore, we analyzed these Pu datasets of reference fallout material in Japan and listed statistical values in Table 1. At present, only limited reference fallout materials have been referenced. It is a great challenge to collect enough fallout material to prepare the reference material since the activity levels are becoming extremely low and there is no long-term observation station to provide a collection place.

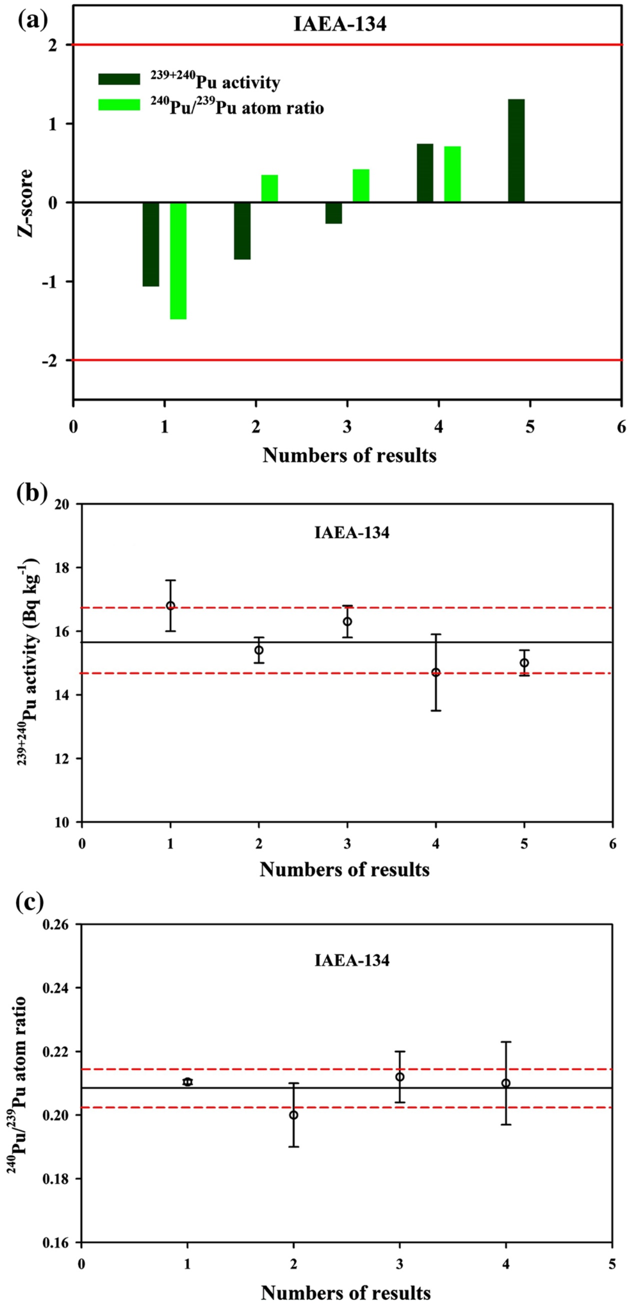

Fig. 6 Distributions of *Z*-scores of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio (**a**) and data evaluation for $^{239+240}$Pu activity (**b**) and ^{240}Pu/^{239}Pu atom ratio (**c**) in IAEA-134. The black solid lines and red dashed lines showed the median value and the corresponding standard deviation, respectively. The error bars correspond to the combined uncertainty reported in the literature. (Color figure online)

Conclusions

We first reviewed over 30 Pu-RMs and prepared many Pu datasets. After statistical analyses, we compiled the statistical values of $^{238-241}$Pu activities and isotopic ratios of Pu (^{238}Pu/$^{239+240}$Pu activity ratios, ^{240}Pu/^{239}Pu atom ratios and

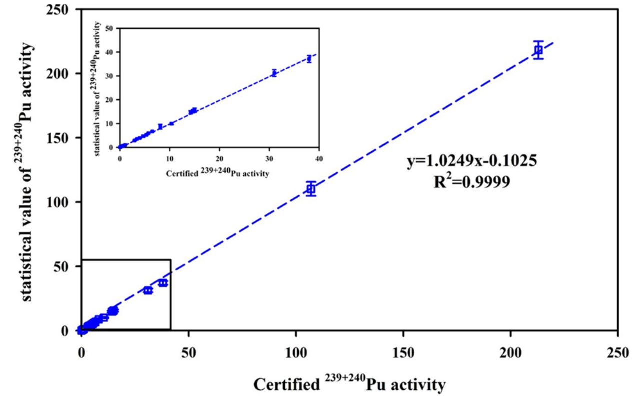

Fig. 7 Relationship between statistical value of $^{239+240}$Pu activity of reference material and its certified $^{239+240}$Pu activity from the approval agencies

^{241}Pu/^{239}Pu atom ratios) for the RMs. Especially, we expect the statistical values of the Pu isotopic ratios will come to fill the gaps in information provided for the RMs by their approval agencies such as IAEA and NIST. The statistical values of $^{239+240}$Pu activity are highly consistent with the certified values from the approval agencies ($R^2 = 0.9999$, Fig. 7), indicating these measured values are highly reliable. Therefore, we expect that through further independent work at different laboratories, the statistical values of Pu isotopic ratios have high reliability. The statistical value of Pu isotopic ratio will also help in establishing a baseline for environmental Pu analysis and provide a way to suitably select RMs. Finally, we point out that Pu isotopic ratios measured in the reference materials will not have the same credentials as the certified values referring to ISO test method or ASTM test method. These statistical values can, at best, be consensus values. Therefore, it is very necessary to produce the matrix matched Pu isotopic standards for quality control of environmental Pu analysis.

Acknowledgements This work was supported by the STU Scientific Research Foundation for Talents (NTF18011), the major special project of Guangdong Laboratory of Southern Marine Science and Engineering (GML2019ZD0606) and the JSPS Kakenhi (Grant Nos. JP17k00537 and JP17H01874).

Author's contribution The manuscript was written with equal contributions from all the authors. All authors have approved the final version of the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Hirose K, Sugimura Y (1990) Plutonium isotopes in the surface air in Japan: effect of Chernobyl accident. J Radioanal Nucl Chem 138:127–138
2. Zheng J, Tagami K, Watanabe Y, Uchida S, Aono T, Ishii N, Yoshida S, Kubota Y, Fuma S, Ihara S (2012) Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident. Sci Rep 2:304. https://doi.org/10.1038/srep00304
3. Kershaw PJ, Woodhead DS, Lovett MB, Leonard KS (1995) Plutonium from European reprocessing operations—its behavior in the marine environment. Appl Radiat Isot 46:1121–1134
4. Dai MH, Kelley JM, Buesseler KO (2002) Sources and migration of plutonium in groundwater at the Savannah River Site. Environ Sci Technol 36:3690–3699
5. Dai MH, Buesseler KO, Pike SM (2005) Plutonium in groundwater at the 100 K-area of the US DOE Hanford site. J Contam Hydrol 76:167–189
6. Harley JH (1980) Plutonium in the environment—a review. J Radiat Res 21:83–104
7. Sholkovitz ER (1983) The geochemistry of plutonium in fresh and marine water environments. Earth Sci Rev 19:95–161
8. Lindahl P, Lee SH, Worsfold P, Keith-Roach M (2010) Plutonium isotopes as tracers for ocean processes: a review. Mar Environ Res 69:73–84
9. Fowler SW, Ballestra S, La Rosa J, Fukai R (1983) Vertical transport of particulate–associated plutonium and americium in the upper water column of the northeast Pacific. Deep-Sea Res Part A 30:1221–1233
10. Livingston HD, Anderson RF (1983) Large particle transport of plutonium and other fallout radionuclides to the deep ocean. Nature 303:228–231
11. Zheng J, Yamada M (2006) Plutonium isotopes in settling particles: transport and scavenging of Pu in the western Northwest Pacific. Environ Sci Technol 40:4103–4108
12. Wu JW, Dai MH, Xu Y, Zheng J (2018) Sources and accumulation of plutonium in a large Western Pacific marginal sea: the South China Sea. Sci Total Environ 610–611:200–211
13. Wu JW, Dai MH, Xu Y, Zheng J (2019) Plutonium in the western North Pacific: transport along the Kuroshio and implication for the impact of the Fukushima Daiichi Nuclear Power Plant accident. Chem Geol 511:256–264
14. Lariviere D, Taylor VF, Evans RD, Cornett RJ (2006) Radionuclide determination in environmental samples by inductively coupled plasma mass spectrometry. Spectrochim Acta, Part B 61:877–904
15. Leon Vintro L, Mitchell PI, Condren OM, Downes AB, Papucci C, Delfanti R (1999) Vertical and horizontal fluxes of plutonium and americium in the western Mediterranean and the Strait of Gibraltar. Sci Total Environ 237–238:77–91
16. Hirose K, Miyao T, Aoyama M, Igarashi Y (2002) Plutonium isotopes in the Sea of Japan. J Radioanal Nucl Chem 252:293–299
17. Wu JW, Zheng J, Dai MH, Huh CA, Chen WF, Tagami K, Uchida S (2014) Isotopic composition and distribution of plutonium in northern South China Sea sediments revealed continuous release and transport of Pu from the Marshall Islands. Environ Sci Technol 48:3136–3144
18. Kelley JM, Bond LA, Beasley TM (1999) Global distribution of Pu isotopes and ^{237}Np. Sci Total Environ 237–238:483–500
19. Huh CA, Pisias NG, Kelley JM, Maiti TC, Grantz A (1997) Natural radionuclides and plutonium in sediments from the western Arctic Ocean: sedimentation rates and pathways of radionuclides. Deep-Sea Res II 44:1725–1743
20. Yamana H, Yamamoto T, Moriyama H (2001) Isotopic ratio of Pu released from fuel cycle facilities—importance of radiochemically pure ^{236}Pu as a tracer. In: Kudo A (ed) Plutonium in the environment. Elsevier, Oxford, pp 31–46
21. Schneider S, Walther C, Bister S, Schauer V, Christl M, Synal HA, Shozugawa K, Steinhauser G (2013) Plutonium release from Fukushima Daiichi fosters the need for more detailed investigations. Sci Rep 3:2988. https://doi.org/10.1038/srep02988
22. Boulyga SF, Erdmann N, Funk H, Kievets MK, Lomonosova EM, Mansel A, Trautmnn N, Yaroshevich OI, Zhuk IV (1997) Determination of isotopic composition of plutonium in hot particles of the Chernobyl area. Radiat Meas 28:349–352
23. Boulyga SF, Becker JS (2002) Isotopic analysis of uranium and plutonium using ICP-MS and estimation of burn-up of spent uranium in contaminated environmental samples. J Anal At Spectrom 17:1143–1147
24. Muramatsu Y, Ruhm W, Yoshida S, Tagami K, Uchida S, Wirth E (2000) Concentrations of ^{239}Pu and ^{240}Pu and their isotopic ratios determined by ICP-MS in soils collected from the Chernobyl 30-km zone. Environ Sci Technol 34:2913–2917
25. Oughton DH, Skipperud L, Fifield LK, Cresswell RG, Salbu B, Day P (2004) Accelerator mass spectrometry measurement of ^{240}Pu/^{239}Pu isotope ratios in Novaya Zemlya and Kara Sea sediments. Appl Radiat Isot 61:249–253
26. Buesseler KO, Halverson JE (1987) The mass spectrometric determination of fallout ^{239}Pu and ^{240}Pu in marine samples. J Environ Radioact 5:425–444
27. Eigl R, Srncik M, Steier P, Wallner G (2013) ^{236}U/^{238}U and ^{240}Pu/^{239}Pu isotopic ratio in small (2 L) sea and river water samples. J Environ Radioact 116:54–58
28. Zheng J, Yamada M (2004) Sediment core record of global fallout and Bikini close-in fallout Pu in Sagami Bay, western Northwest Pacific margin. Environ Sci Technol 38:3498–3504
29. Zheng J, Yamada M (2005) Vertical distributions of $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in sediment cores: implications for the sources of Pu in the Japan Sea. Sci Total Environ 340:199–211
30. Wang ZT, Zheng J, Ni YY, Men W, Tagami K, Uchida S (2017) High-performance method for determination of Pu isotopes in soil and sediment samples by sector field-inductively coupled plasma mass spectrometry. Anal Chem 89:2221–2226
31. Lindahl P, Keith-Roach M, Worsfold P, Choi MS, Shin HS, Lee SH (2010) Ultra-trace determination of plutonium in marine samples using multi-collector inductively coupled plasma mass spectrometry. Anal Chim Acta 671:61–69
32. Mathew KJ, Stanley FE, Thomas MR, Spencer KJ, Colletti LM, Tandon L (2016) Critical need for plutonium and uranium isotopic standards with lower uncertainties. Anal Methods 8:7289–7305
33. Buesseler KO (1997) The isotopic signature of fallout plutonium in the North Pacific. J Environ Radioact 36:69–83
34. International Organization for Standardization (ISO) (1992) Guide 30 "terms and definitions used in connection with reference materials". ISO, Geneva
35. Povinec PP, Pham MK, Sanchez-Cabeza JA, Barci-Funel G, Bojanowski R, Boshkova T, Burnett WC, Carvalho F, Chapeyron B, Cunha IL, Dahlgaard H, Galabov N, Fifield LK, Gastaud J, Geering JJ, Gomez IF, Green N, Hamilton T, Ibanez FL, Ibn-Majah M, John M, Kanisch G, Kenna TC, Kloster M, Korun M, Liong Wee Kwong L, La Rosa J, Lee SH, Levy-Palomo I, Malatova M, Maruo Y, Mitchell P, Murciano IV, Nelson R, Nouredine A, Oh JS, Oregioni B, Le Petit G, Pettersson HBL, Reineking A, Smedley PA, Suckow A, Van der Struijs TDB, Voors PI, Yoshimizu K, Wyse E (2007) Reference material for radionuclides in sediment IAEA-384 (Fangataufa Lagoon sediment). J Radioanal Nucl Chem 273:383–393

36. Godoy MLDP, Godoy JM, Tauhata LA, Tauhata L (2009) Determination of total content and isotopic compositions of plutonium and uranium in environmental samples for safeguards purposes by ICP-MS. J Environ Radioact 100:613–625
37. Lindahl P, Worsfold P, Keith-Roach M, Andersen MB, Kershaw P, Leonard K, Choi MS, Boust D, Lesueur P (2011) Temporal record of Pu isotopes in inter-tidal sediments from the northeastern Irish Sea. Sci Total Environ 409:5020–5025
38. Pham MK, Sanchez-Cabeza JA, Povinec PP, Andor K, Arnold D, Benmansour M, Bikit I, Carvalho FP, Dimitrova K, Edrev ZH, Engeler C, Fouche FJ, Garcia-Orellana J, Gasco C, Gastaud J, Gudelis A, Hancock G, Holm E, Legarda F, Ikaheimonen TK, Ilchmann C, Jenkinson AV, Kanisch G, Kis-Benedek G, Kleinschmidt R, Koukouliou V, Kuhar B, La Rosa J, Lee SH, LePetit G, Levy-Palomo I, Liong Wee Kwong L, Llaurado M, Maringer FJ, Meyer M, Michalik B, Michel H, Nies H, Nour S, Oh JS, Oregioni B, Palomares J, Pantelic G, Pfitzner J, Pilvio R, Puskeiler L, Satake H, Schikowski J, Vitorovic G, Woodhead D, Wyse E (2008) A new certified reference material for radionuclides in Irish Sea sediment (IAEA–385). Appl Radiat Isot 66:1711–1717
39. Mathew KJ, O'Connor G, Hasozbek A, Kraiem M (2013) Total evaporation method for uranium isotope-amount ratio measurements. J Anal At Spectrom 28:866–876
40. Mathew KJ, Essex RM, Gradle C, Narayanan U (2015) Uncertainties achievable for uranium isotope-amount ratios: estimates based on the precision and accuracy of recent characterization measurements. J Radioanal Nucl Chem 305:277–282
41. Mathew KJ, Ottenfeld C, Keller R, Slemmons A (2018) Systematic bias in the ^{240}Pu/^{239}Pu isotope ratio of Plutonium isotopic standard CRM138. J Radioanal Nucl Chem 318:395–400
42. International Organization of Standardization (ISO) (1993) Guide 98 "Guide to the expression of uncertainty in measurement". ISO, Geneva
43. Taylor BN, Kuyatt CE (1994) Guidelines for evaluating and expressing the uncertainty of NIST measurement results. NIST technical note 1297, Washington DC, p 20
44. International Organization for Standardization (ISO) (1997) Guide 43 "Proficiency testing and interlaboratory comparisons". ISO/IEC, Geneva
45. Thompson M, Ellison SLR, Wood R (2006) The international harmonized protocol for the proficiency testing of analytical chemistry laboratories. J Pure Appl Chem 78:145–196
46. Cofino WP, Wells DE (1994) Design and evaluation of the QUASIMEME inter-laboratory performance studies: a test case for robust statistics. Mar Pollut Bull 29:149–158
47. FAPAS (2002) Protocol for the food analysis performance assessment scheme, organization and analysis of data, 6th edn. Central Science Laboratory, York
48. Pham-Gia T, Hung TL (2001) The mean and median absolute deviations. Math Comput Model 34:921–936
49. Lee SH, Gastaud J, La Rosa J, Liong Wee Kwong L, Povinec PP, Wyse E, Fifield LK, Hausladen PA, Di Tada LM, Santos GM (2001) Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques. J Radioanal Nucl Chem 248:757–764
50. Croudace I, Warwick P, Taylor R, Dee S (1998) Rapid procedure for plutonium and uranium determination in soils using a borate fusion followed by ion–exchange and extraction chromatography. Anal Chim Acta 371:217–225
51. Muramatsu Y, Uchida S, Tagami K, Yoshida S, Fujikawa T (1999) Determination of plutonium concentration and its isotopic ratio in environmental materials by ICP-MS after separation using ion-exchange and extraction chromatography. J Anal At Spectrom 14:859–865
52. Mellado J, Llauradó M, Rauret G (2001) Determination of Pu, Am, U, Th and Sr in marine sediment by extraction chromatography. Anal Chim Acta 443:81–90
53. Kenna TC (2002) Determination of plutonium isotopes and neptunium-237 in environmental samples by inductively coupled plasma mass spectrometry with total sample dissolution. J Anal At Spectrom 17:1471–1479
54. Nygren U, Rodushkin I, Nilsson C, Baxter DC (2003) Separation of plutonium from soil and sediment prior to determination by inductively coupled plasma mass spectrometry. J Anal At Spectrom 18:1426–1434
55. Tavcar P, Jakopic R, Benedik L (2005) Sequential determination of ^{241}Am, ^{237}Np, Pu radioisotopes and 90Sr in soil and sediment samples. Acta Chim Slov 52:60–66
56. Taddei MHT, Silva NC (2006) Radiochemical procedure for the determination of plutonium isotopes in powdered milk. J Radioanal Nucl Chem 269(2):457–461
57. Al-Rayyes AH, Al-Oudat M, Al-Hamwi A, Mukhallalati H (2007) Behavior of ^{134}Cs, ^{90}Sr, and ^{238}Pu in different Syrian soils. J Radioanal Nucl Chem 274(1):139–143
58. Donard OFX, Bruneau F, Moldovan M, Garraud H, Epov VN, Boust D (2007) Multi-isotopic determination of plutonium (^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) in marine sediments using sector-field inductively coupled plasma mass spectrometry. Anal Chim Acta 587:170–179
59. Godoy MLDP, Godoy JM, Roldao LA (2007) Application of ICP-QMS for the determination of plutonium in environmental samples for safeguards purposes. J Environ Radioact 97:124–136
60. Child DP, Hotchkis MAC, Williams ML (2008) High sensitivity analysis of plutonium isotopes in environmental samples using accelerator mass spectrometry (AMS). J Anal At Spectrom 23:765–768
61. Hrnecek E, Jakopic R, Wallner A, Steier P (2008) A combined method for the determination of the isotopic vector of plutonium isotopes in environmental samples. J Radioanal Nucl Chem 276(3):789–793
62. Qiao JX, Hou XL, Roos P, Miró M (2011) Rapid isolation of plutonium in environmental solid samples using sequential injection anion exchange chromatography followed by detection with inductively coupled plasma mass spectrometry. Anal Chim Acta 685:111–119
63. Oh JS, Warwick PE, Croudace IW, Lee SH (2013) Rapid measurement of ^{241}Pu activity at environmental levels using low-level liquid scintillation analysis. J Radioanal Nucl Chem 298:353–359
64. Kim CS, Kim CK, Lee JI, Lee KJ (2000) Rapid determination of Pu isotopes and atom ratios in small amounts of environmental samples by an on-line sample pre-treatment system and isotope dilution high resolution inductively coupled plasma mass spectrometry. J Anal At Spectrom 15:247–255
65. Ohtsuka Y, Takaku Y, Kimura J, Hisamatsu S, Inaba J (2005) Development of rapid Plutonium analysis for environmental samples by isotope dilution/inductively coupled plasma mass spectrometry with on-line column. Anal Sci 21:205–208
66. Zheng J, Yamada M (2006) Determination of Pu isotopes in sediment cores in the Sea of Okhotsk and the NW Pacific by sector field ICP-MS. J Radioanal Nucl Chem 267(1):73–83
67. Figueira RCL, Tessler MG, de Mahiques MM, Cunha IIL (2007) Distribution of ^{137}Cs, ^{238}Pu and $^{239+240}$Pu in sediments of the southeastern Brazilian shelf-SW Atlantic margin. Sci Total Environ 357:146–159
68. Liao HQ, Zheng J, Wu FC, Yamada M, Tan M, Chen JM (2008) Determination of plutonium isotopes in freshwater lake sediments by sector-field ICP-MS after separation using ion-exchange chromatography. Appl Radiat Isot 66:1138–1145

69. Michel H, Levent D, Barci V, Barci-Funel G, Hurel C (2008) Soil and sediment sample analysis for the sequential determination of natural and anthropogenic radionuclides. Talanta 74:1527–1533
70. Zhang YS, Zheng J, Yamada M, Wu FC, Igarashi Y, Hirose K (2010) Characterization of Pu concentration and its isotopic composition in a reference fallout material. Sci Total Environ 408:1139–1144
71. Liu ZY, Zheng J, Yamada M, Pan SM, Kawahata H (2011) Plutonium characteristics in sediments of Hiroshima Bay in the Seto Inland Sea in Japan. J Radioanal Nucl Chem 288:911–917
72. Wu FC, Zheng J, Liao HQ, Yamada M, Wan GJ (2011) Anomalous plutonium isotopic ratios in sediments of lake Qinghai from the Qinghai–Tibetan Plateau, China. Environ Sci Technol 45:9188–9194
73. Bu WT, Zheng J, Aono T, Tagami K, Uchida S, Zhang J, Honda MC, Guo QJ, Yamada M (2013) Vertical distributions of plutonium isotopes in marine sediment cores off the Fukushima coast after the Fukushima Dai-ichi nuclear power plant accident. Biogeosciences 10:2497–2511
74. Bu WT, Zheng J, Guo QJ, Aono T, Tazoe H, Tagami K, Uchida S, Yamada M (2014) A method of measurement of ^{239}Pu, ^{240}Pu, ^{241}Pu in high U content marine sediments by sector field ICP-MS and its application to Fukushima sediment samples. Environ Sci Technol 48:534–541
75. Bu WT, Zheng J, Guo QJ, Xiao DT, Aono T (2017) Determination of Pu isotopes in sediment and soil samples by SF-ICP-MS: an improved anion-exchange procedure for Pu separation. J Radioanal Nucl Chem 314:2417–2423
76. Sahli H, Röllin S, Putyrskaya V, Klemt E, Balsiger B, Burger M, Alvarado JAC (2017) A procedure for the sequential determination of radionuclides in soil and sediment samples. J Radioanal Nucl Chem 314:2209–2218
77. Povinec PP, Pham MK (2000) Report on the intercomparison run IAEA-384. Radionuclides in Fangataufa lagoon sediment (No. IAEA-AL--126). International Atomic Energy Agency. Vienna
78. Lee SH, La Rosa J, Gastaud J, Povinec PP (2005) The development of sequential separation methods for the analysis of actinides in sediments and biological materials using anion-exchange resins and extraction chromatography. J Radioanal Nucl Chem 263(2):419–425
79. Varga Z, Surányi G, Vajda N, Stefánka Z (2007) Improved sample preparation method for environmental plutonium analysis by ICP-SFMS and alpha-spectrometry. J Radioanal Nucl Chem 274(1):87–94
80. Varga B, Tarjan S, Vajda N (2008) Plutonium isotopes in the Hungarian environment. J Environ Radioact 99:641–648
81. Lindahl P, Asami R, Iryu Y, Worsfold P, Keith-Roach M, Choi MS (2011) Sources of plutonium to the tropical Northwest Pacific Ocean (1943–1999) identified using a natural coral archive. Geochim Cosmochim Acta 75:1346–1356
82. Lindahl P, Andersen MB, Keith-Roach M, Worsfold P, Hyeong K, Choi MS, Lee SH (2012) Spatial and temporal distribution of Pu in the Northwest Pacific Ocean using modern coral archives. Environ Int 40:196–201
83. Kazi ZH, Cornett RJ, Zhao XL, Kieser L (2014) Americium and plutonium separation by extraction chromatography for determination by accelerator mass spectrometry. Anal Chim Acta 829:75–80
84. Popov L (2019) Determination of plutonium isotopes in environmental samples by extraction chromatography with triisooctylamine-polyethylene resin. Appl Radiat Isot 146:48–56
85. Inn KGW, Lin ZC, Wu ZY, McMahon C, Filliben JJ, Krey P, Feiner M, Liu CK, Holloway R, Harvey J, Larsen IL, Beasley T, Huh CA, Morton S, McCurdy D, Germain P, Handl J, Yamamoto M, Warren B, Bates TH, Holms A, Harvey BR, Popplewell DS, Woods MJ, Jerome S, Odell KJ, Young P, Croudace I (2001) The NIST natural-matrix radionuclide standard reference material program for ocean studies. J Radioanal Nucl Chem 248:227–231
86. Kim CK, Kim CS, Chang BU, Choi SW, Chung CS, Hong GH, Hirose K, Igarashi Y (2004) Plutonium isotopes in seas around the Korean Peninsula. Sci Total Environ 318:197–209
87. Cizdziel JV, Ketterer ME, Farmer D, Faller SH, Hodge VF (2008) ^{239,240,241}Pu fingerprinting of plutonium in western US soils using ICPMS: solution and laser ablation measurements. Anal Bioanal Chem 390:521–530
88. Yoshida S, Muramatsu Y, Yamazaki S, Ban-nai T (2007) Distribution of nuclear bomb Pu in Nishiyama area, Nagasaki, estimated by accurate and precise determination of ^{240}Pu/^{239}Pu ratio in soils. J Environ Radioact 96:85–93
89. Ketterer ME, Szechenyi SC (2008) Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: a historical perspective and new frontiers in the environmental sciences. Spectrochim Acta B 63:719–737
90. Matteson BS, Hanson SK, Miller JL, Oldham-Jr WJ (2015) Concurrent determination of ^{237}Np and Pu isotopes using ICP-MS: analysis of NIST environmental matrix standard reference materials 4357, 1646a, and 2702. J Environ Radioact 142:62–67
91. Huang ZY, Ni YY, Wang H, Zheng J, Yamazaki S, Sakaguchi A, Long XG, Uchida S (2019) Simultaneous determination of ultra-trace level ^{237}Np and Pu isotopes in soil and sediment samples by SF-ICP-MS with a single column chromatographic separation. Microchem J 148:597–604
92. Leon Vintro L, Mitchell PI, Condren OM, Moran M, Vives i Batlle J, Sanchez-Cabeza JA (1996) Determination of the ^{240}Pu/^{239}Pu atom ratio in low activity environmental samples by alpha spectrometry and spectral deconvolution. Nucl Instrum Methods Phys Res, Sect A 369:597–602
93. McAninch JE, Hamilton TF, Brown TA, Jokela TA, Knezovich JP, Ognibene TJ, Proctor ID, Roberts ML, Sideras-Haddad E, Southon JR, Vogel JS (2000) Plutonium measurements by accelerator mass spectrometry at LLNL. Nucl Instrum Methods Phys Res, Sect B 172:711–716
94. Wyse EJ, Lee SH, La Rosa J, Povinec P, de Mora SJ (2001) ICP-sector field mass spectrometry analysis of plutonium isotopes: recognizing and resolving potential interferences. J Anal At Spectrom 16:1107–1111
95. Kim CS, Kim CK, Lee KJ (2004) Simultaneous analysis of ^{237}Np and Pu isotopes in environmental samples by ICP-SF-MS coupled with automated sequential injection system. J Anal At Spectrom 19:743–750
96. Choi MS, Lee DS, Choi JC, Cha HJ, Yi HI (2006) $^{239+240}$Pu concentration and isotope ratio (^{240}Pu/^{239}Pu) in aerosols during high dust (Yellow Sand) period, Korea. Sci Total Environ 370:262–270
97. Jakopic R, Richter S, Kuehn H, Aregbe Y (2010) Determination of ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotope ratios in environmental reference materials and samples from Chernobyl by thermal ionization mass spectrometry (TIMS) and filament carburization. J Anal At Spectrom 25:815–821
98. Jakopic R, Sturm M, Kraiem M, Richter S, Aregbe Y (2013) Certified reference materials and reference methods for nuclear safeguards and security. J Environ Radioact 125:17–22
99. Gray J, Jones SR, Smith AD (1995) Discharges to the environment from the Sellafield site, 1951–1992. J Radiol Prot 15:99–131
100. Shibahara Y, Kubota T, Fujii T, Fukutani S, Takamiya K, Konno M, Mizuno S, Yamana H (2016) Determination of isotopic ratios of plutonium and uranium in soil samples by thermal ionization mass spectrometry. J Radioanal Nucl Chem 307(3):2281–2287

101. Ohtsuka Y, Aoyama M, Takaku Y, Igarashi Y, Hattori M, Hirose K, Hisamatsu S (2019) $^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ atom ratio of Japanese monthly atmospheric deposition samples during 1963–1966. Sci Rep 9:8105. https://doi.org/10.1038/s41598-019-44352-7
102. Greis C, Karlsson S, Düker A, Pettersson HBL, Allard B (2008) Determination of plutonium in environmental samples with quadrupole ICP-MS. J Radioanal Nucl Chem 275(1):55–70
103. Povinec PP, Woodhead D, Blowers P, Bonfield R, Cooper M, Chen QJ, Dahlgaard H, Dovlete C, Fox V, Froehlich K, Gastaud J, Groning M, Hamilton T, Ikeuchi Y, Kanisch G, Kruger A, Kwong LLW, Matthews M, Morgenstern U, Mulsow S, Pettersson H, Smedley P, Taylor B, Taylor C, Tinker R (1999) Marine radioactivity assessment of Mururoa and Fangataufa atolls. Sci Total Environ 237–238:249–267
104. Sturup S, Dahlgaard H, Nielsen SC (1998) High resolution inductively coupled plasma mass spectrometry for the trace determination of plutonium isotopes and isotope ratios in environmental samples. J Anal At Spectrom 13:1321–1326
105. Povinec PP, Pham MK (2001) IAEA reference materials for quality assurance of marine radioactivity measurements. J Radioanal Nucl Chem 248:211–216
106. Kim CS, Kim CK, Lee KJ (2002) Determination of Pu isotopes in seawater by an on-line sequential injection technique with sector field inductively coupled plasma mass spectrometry. Anal Chem 74:3824–3832
107. La Rosa J, Gastaud J, Lagan L, Lee SH, Levy-Palomo I, Povinec PP, Wyse E (2005) Recent developments in the analysis of transuranics (Np, Pu, Am) in seawater. J Radioanal Nucl Chem 263:427–436
108. Zheng J, Yamada M (2007) Precise determination of Pu isotopes in a seawater reference material using ID-SF-ICP-MS combined with two-stage anion-exchange chromatography. Anal Sci 23:611–615
109. Chamizo E, Enamorado SM, Garcia-Leon M, Suter M, Wacker L (2008) Plutonium measurements on the 1 MV AMS system at the Centro National de Aceleradores (CNA). Nucl Instrum Methods Phys Sect B 266:4948–4954
110. Levy I, Povinec PP, Aoyama M, Hirose K, Sanchez-Cabeza JA, Comanducci JF, Gastaud J, Eriksson M, Hamajima Y, Kim CS, Komura K, Osvath I, Roos P, Yim SA (2011) Marine anthropogenic radiotracers in the Southern Hemisphere: new sampling and analytical strategies. Prog Oceanogr 89:120–133
111. Pham MK, Betti M, Povinec PP, Benmansour M, Bunger V, Drefvelin J, Engeler C, Flemal JM, Gasco C, Guillevic J, Gurriaran R, Groening M, Happel JD, Herrmann J, Klemola S, Kloster M, Kanisch G, Leonard K, Long S, Nielsen S, Oh JS, Rieth PU, Ostergren I, Pettersson H, Pinhao N, Pujol L, Sato K, Schikowski J, Varga Z, Vartti VP, Zheng J (2011) A certified reference material for radionuclides in the water sample from Irish Sea (IAEA-443). J Radioanal Nucl Chem 288:603–611
112. Bu WT, Zheng J, Guo QJ, Aono T, Tagami K, Uchida S, Tazoe H, Yamada M (2014) Ultra-trace plutonium determination in small volume seawater by sector field inductively coupled plasma mass spectrometry with application to Fukushima seawater samples. J Chromatogr A 1337:171–178
113. Zheng J, Yamada M (2012) Determination of plutonium isotopes in seawater reference materials using isotope-dilution ICP-MS. Appl Radiat Isot 70:1944–1948
114. Wang ZT, Lin JX, Li SX, Guo QJ, Huang WN, Wen W, Dan GP, Tan ZY (2018) Rapid method for accurate determination of actinides (U, Th, Pu and Am) in water samples for emergency response. J Radioanal Nucl Chem 315:103–110
115. Lopez-Lora M, Chamizo E (2019) Accelerator mass spectrometry of ^{237}Np, ^{239}Pu and ^{240}Pu for environmental studies at the Centro Nacional de Aceleradores. Nucl Instrum Methods Phys Res B 455:39–51
116. Norisuye K, Okamura K, Sohrin Y, Hasegawa H, Nakanishi T (2006) Large volume preconcentration and purification for determining the $^{240}Pu/^{239}Pu$ isotopic ratio and $^{238}Pu/^{239+240}Pu$ alpha-activity ratio in seawater. J Radioanal Nucl Chem 267:183–193
117. Quinto F, Golser R, Lagos M, Plaschke M, Schafer T, Steier P, Geckeis H (2015) Accelerator mass spectrometry of actinides in ground- and seawater: an innovative method allowing for the simultaneous analysis of U, Np, Am, and Cm isotopes below ppq levels. Anal Chem 87:5766–5773
118. Men W, Zheng J, Wang H, Ni YY, Kumamoto Y, Yamada M, Uchida S (2019) Pu isotopes in the seawater off Fukushima Daiichi nuclear power plant site within two months after the severe nuclear accident. Environ Pollut 246:303–310
119. Cao LG, Bu WT, Zheng J, Pan SM, Wang ZT, Uchida S (2016) Plutonium determination in seawater by inductively coupled plasma mass spectrometry: a review. Talanta 151:30–41
120. Otsuji-Hatori M, Igarashi Y, Hirose K (1996) Preparation of a reference fallout material for activity measurements. J Environ Radioact 31:143–155
121. Ballestra S, Gastaud J, Lopez JJ, Parsi P, Vas D (2000) Reference material IAEA-135. Radionuclides in Irish sea sediment. Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
122. Toribio M, García JF, Rauret G, Pilviö R, Bickel M (2001) Plutonium determination in mineral soils and sediments by a procedure involving microwave digestion and extraction chromatography. Anal Chim Acta 447:179–189
123. Kwong LLW, Gastaud J, La Rosa J, Lee SH, Povinec PP, Wyse E (2004) Determination of ^{241}Pu in marine samples using coprecipitation with rare earth fluoride and liquid scintillation spectrometry. J Radioanal Nucl Chem 261(2):283–289
124. Tavcar P, Smodis B, Benedik L (2007) Radiological characterization of low- and intermediate-level radioactive wastes. J Radioanal Nucl Chem 273(3):593–596
125. Ballestra S, Gastaud J, Lopez JJ, Parsi P, Vas D (2000) Reference material IAEA–300. Radionuclides in basaltic sea sediment, Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
126. Lin XJ, Park G, Kwak JH, Kim W, Kang HD, Lee HL, Kim YG, Doh SH, Kim DS, Kim CK (2006) $^{239+240}Pu$ concentrations of sediments and seawater in the coastal sea of Korea. J Radioanal Nucl Chem 268(1):103–108
127. Lee MH, Ahn HJ, Park JH, Park YJ, Song K (2011) Rapid sequential determination of Pu, ^{90}Sr and ^{241}Am nuclides in environmental samples using an anion exchange and Sr-Spec resins. Appl Radiat Isot 69:295–298
128. Lee MS, Park TH, Park JH, Song K (2013) Radiochemical separation of Pu, U, Am and Sr isotopes in environmental samples using extraction chromatographic resins. J Radioanal Nucl Chem 295:1419–1422
129. Nygren U, Rodushkin I, Nilsson C, Baxter DC (2013) Separation of plutonium from soil and sediment prior to determination by inductively coupled plasma mass spectrometry. J Anal At Spectrom 18:1426–1434
130. Skrzypiec B, Jodlowski P, Mietelski JW (2013) Plutonium in Gorce Mountains area (Southern Poland). J Radioanal Nucl Chem 295:771–775
131. Kang DJ, Chung CS, Kim SH, Kim KR, Hong GH (1997) Distribution of ^{137}Cs and $^{239,240}Pu$ in the surface waters of the East Sea (Sea of Japan). Mar Pollut Bull 35:305–312
132. Ballestra S (1988) Reference material IAEA–307. Radionuclides in seaplants, Reference sheet, International Atomic

Energy Agency. Analytical Quality Control Services, Vienna, Austria

133. Shinonaga T, Aigner H, Klose D, Spinder P, Froschl H, Donohu D (2008) Recommended values of 239Pu, 240Pu and 239 + 240Pu concentrations in reference material IAEA-315 (marine sediment) estimated by thermal ionization mass spectrometry, inductively coupled plasma-mass spectrometry and alpha spectrometry. Geostand Geoanal Res 32:93–101
134. Lee MH, Pimpl M (1999) Development of a new electrodeposition method for Pu-determination in environmental samples. Appl Radiat Isot 50:851–857
135. Bojanowski R, Radecki Z, Campbell MJ, Burns KI, Trinkl A (2001) Report on the intercomparison run for the determination of radionuclides in soils. IAEA-326 (No. IAEA-AL--100). International Atomic Energy Agency
136. Bojanowski R, Radecki Z, Campbell MJ, Burns KI, Trinkl A (2001) Report on the intercomparison run for the determination of radionuclides in soils. IAEA-327 (No. IAEA-AL--100). International Atomic Energy Agency
137. Lokas E, Mietelski JW, Ketterer ME, Kleszcz K, Wachniew P, Michalska S, Miecznik M (2013) Sources and vertical distribution of ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{241}Am in peat profiles from southwest Spitsbergen. Appl Geochem 28:100–108
138. Ballestra S, Lopez JJ, Gastaud J, Vas D, Noshkin V (2000) Reference material IAEA–367. Radionuclides in Pacific Ocean Sediment. Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
139. Nygren U, Rameback H, Nilsson C (2007) Age determination of plutonium using inductively coupled plasma mass spectrometry. J Radioanal Nucl Chem 272:45–51
140. Martinelli RE, Hamilton TF, Williams RW, Kehl SR (2009) Separation of uranium and plutonium isotopes for measurement by multi collector inductively coupled plasma mass spectroscopy. J Radioanal Nucl Chem 282:343–347
141. Xu YH, Qiao JX, Hou XL, Pan SM, Roos P (2014) Determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) in environmental samples using radiochemical separation combined with radiometric and mass spectrometric measurements. Talanta 119:590–595
142. Ballestra S, Lopez JJ, Gastaud J, Parsi P, Vas D, Noshkin V (2000) Reference material IAEA–368. Radionuclides in Pacific Ocean Sediment. Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
143. Radecki Z, Campbell M.J, Burns K.I (2000) Reference Material IAEA–375. Radionuclides and trace elements in soil. Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
144. Mietelski JW, Kitowski I, Gaca P, Grabowska S, Tomankiewicz E, Szwalko P (2006) Gamma-emitters ^{90}Sr, $^{238,239+240}$Pu and ^{241}Am in bones and liver of eagles from Poland. J Radioanal Nucl Chem 270(1):131–135
145. Epov VN, Evans RD, Zheng J, Donard OFX, Yamada M (2007) Rapid fingerprinting of ^{239}Pu and ^{240}Pu in environmental samples with high U levels using on-line ion chromatography coupled with high-sensitivity quadrupole ICP-MS detection. J Anal At Spectrom 22:1131–1137
146. AlKheliewi AS, Shabana EI (2007) Activity concentration of some anthropogenic radionuclides in the surface marine sediments near the Saudi coast of the Arabian (Persian) Gulf. J Radioanal Nucl Chem 274:207–212
147. Popov L, Mihailova G, Naidenov I (2010) Determination of activity ratios of $^{238,239+240,241}$Pu, ^{241}Am, ^{134,137}Cs and ^{90}Sr in Bulgarian soils. J Radioanal Nucl Chem 285:223–237
148. Cao LG, Zheng J, Tsukada H, Pan SM, Wang ZT, Tagami K, Uchida S (2016) Simultaneous determination of radiocesium (^{135}Cs, ^{137}Cs) and plutonium (^{239}Pu, ^{240}Pu) isotopes in river suspended particles by ICP-MS/MS and SF-ICP-MS. Talanta 159:55–63
149. Varga B, Tarjan S (2008) Determination of ^{241}Pu in the environmental samples. Appl Radiat Isot 66:265–270
150. Pham MK, Sanchez-Cabeza JA, Povinec PP (2005) Report on the worldwide intercomparison exercise—IAEA-385, radionuclides in irish sea sediment, pp 1–76
151. Qiao JX, Hou XL, Roos P, Miro M (2011) High-throughput sequential injection method for simultaneous determination of plutonium and neptunium in environmental solids using microporous anion-exchange chromatography, followed by inductively coupled plasma mass spectrometric detection. Anal Chem 83:374–381
152. Landstetter C, Damberger V, Zapletal M, Katzlberger C (2015) Development of a rapid method to determine plutonium in foodstuffs. J Radioanal Nucl Chem 304:343–347
153. Xing S, Zhang WZ, Qiao JX, Hou XL (2018) Determination of ultra-low level plutonium isotopes (^{239}Pu, ^{240}Pu) in environmental samples with high uranium. Talanta 187:357–364
154. Pham MK, van Beek PV, Carvalho FP, Chamizo E, Degering D, Engeler C, Gasco C, Gurriaran R, Hanley O, Harms AV, Herrmann J, Hult M, Ikeuchi Y, Ilchmann C, Kanisch G, Kis-Benedek G, Kloster M, Laubenstein M, Llaurado M, Mas JL, Nakano M, Nielsen SP, Osvath I, Povinec PP, Rieth U, Schikowski J, Smedley PA, Suplinska M, Sykora I, Tarjan S, Varga B, Vasileva E, Zalewska T, Zhou W (2016) Certified reference materials for radionuclides in Bikini Atoll sediment (IAEA-410) and Pacific Ocean sediment (IAEA-412). Appl Radiat Isot 109:101–104
155. Vasile M, Jacobs K, Bruggeman M, Van Hoecke K, Dobney A, Verrezen F (2018) On the sequential separation and quantification of ^{237}Np, ^{241}Am, thorium, plutonium, and uranium isotopes in environmental and urine samples. Appl Radiat Isot 134:455–460
156. Shakhashiro A, Tarjan S, Ceccatelli A, Kis-Benedek G, Betti M (2012) IAEA-447: a new certified reference material for environmental radioactivity measurements. Appl Radiat Isot 70:1632–1643
157. Park TH, Jeon EH, Choi YS, Park JH, Ahn HJ, Park YJ (2016) Rapid quantification of alpha emitters in low- and intermediate-level dry radioactive waste. J Radioanal Nucl Chem 307:645–651
158. Radecki Z, Campbell MJ, Trinkl A, Burns KI (1999) Reference material IAEA–Soil–6. Radionuclides in soil. Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
159. Danesi PR, Bleise A, Burkart W, Cabianca T, Campbell MJ, Makarewicz M, Moreno J, Tuniz C, Hotchkis M (2003) Isotopic composition and origin of uranium and plutonium in selected soil samples collected in Kosovo. J Environ Radioact 64:121–131
160. Agarande M, Benzoubir S, Neiva-Marques AM, Bouisset P (2004) Sector field inductively coupled plasma mass spectrometry, another tool for plutonium isotopes and plutonium isotope ratios determination in environmental matrices. J Environ Radioact 72:169–176
161. Komosa A, Chibowski S, Kitowski I, Krawczyk R, Orzel J, Reszka M (2006) Transfer of selected heavy metals and radionuclides from calcareous peat to saw sedge (Cladium mariscus) in eastern Poland. J Radioanal Nucl Chem 269(1):195–201
162. Faghihian H, Rahi D, Mostajaboddavati M (2012) Study of natural radionuclides in Karun river region. J Radioanal Nucl Chem 292:711–717
163. Bu WT, Guo QJ, Zheng J, Uchida S (2017) Plutonium concentration and ^{240}Pu/^{239}Pu isotopic ratio in the surface soils from the Jiuquan region in northwestern China. J Radioanal Nucl Chem 311:999–1005

164. Kuehl SA, Ketterer ME, Miselis JL (2012) Extension of $^{239+240}$Pu sediment geochronology to coarse-grained marine sediment. Contin Shelf Res. 36:83–88
165. Helal I, Zahran NF, Amr MA, El-Lateef AMA, Bashter II, Mohsen HT, Abbas Y (2004) Ultratrace and isotope ratios analyses of some radionuclides by ICP-MS. Radiochim Acta 92:369–374
166. Povinec PP, Pham MK, Ballestra S (2000) Reference material IAEA–381, Radionuclides in Irish Sea Water. Reference sheet, International Atomic Energy Agency. Analytical Quality Control Services, Vienna, Austria
167. Povinec PP, Badie C, Baeza A, Barci-Funel G, Bergan TD, Bojanowski R, Burnett WC, Eikenberg J, Fifield LK, Serradell V, Gastaud J, Goroncy I, Herrmann J, Hotchkis MAC, Ikaheimonen TK, Jakobson E, Kalimbadjan J, La Rosa J, Lee SH, Liong WKL, Lueng WM, Nielsen SP, Noureddine A, Pham MK, Rohou JN, Sanchez-Cabeza JA, Suomela J, Suplinska M, Wyse E (2002) Certified reference material for radionuclides in seawater IAEA-381 (Irish Sea water). J Radioanal Nucl Chem 251(3):369–374
168. Hain K, Faestermann T, Famulok N, Fimiani L, Gomez-Guzman JM, Korschinek G, Kortmann K, Gostomski CLV, Ludwig P, Shinonaga T (2015) Analytical method for the determination of Np and Pu in sea water by AMS with respect to the Fukushima accident. Nucl Instr Meth Phys Res B. 361:505–509
169. Warneke T, Croudace IW, Warwick PE, Taylor RN (2002) A new ground-level fallout record of uranium and plutonium isotopes for northern temperate latitudes. Earth Planet Sci Lett. 203:1047–1057
170. Povinec PP, Lee SH, La Rosa J, Pham MK (2004) Report on the worldwide intercomparison – IAEA–414, Radionuclides in mixed fish from Irish Sea and North Sea MEAAZ/145, MEA/MEZ/73. International Atomic Energy Agency, Monaco
171. Pham MK, Sanchez-Cabeza JA, Povinec PP, Arnold D, Benmansour M, Bojanowski R, Carvalho FP, Kim CK, Esposito M, Gastaud J, Gasco CL, Ham GL, Hegde AG, Holm E, Jaskierowicz D, Kanisch G, Llaurado M, La Rosa J, Lee SH, Liong Wee Kwong L, Le Petit G, Maruo Y, Nielsen SP, Oh JS, Oregioni B, Palomares J, Pettersson HBL, Rulik P, Ryan TP, Sato K, Schikowski J, Skwarzec B, Smedley PA, Tarjan S, Vajda N, Wyse E (2006) Certified reference material for radionuclides in fish flesh sample IAEA-414 (mixed fish from the Irish Sea and North Sea). Appl Radiat Isot 64:1253–1259
172. Pham MK, Benmansour M, Carvalho FP, Chamizo E, Degering D, Engeler C, Gasco C, Gwynn JP, Harms AV, Hrnecek E, Ibanez FL, Ilchmann C, Ikaheimonen T, Kanisch G, Kloster M, Llaurado M, Mauring A, Moller B, Morimoto T, Nielsen SP, Nies H, Norrlid LDR, Pettersson HBL, Povinec PP, Rieth U, Samuelsson C, Schikowski J, Silobritiene BV, Smedley PA, Suplinska M, Vartti VP, Vasileva E, Wong J, Zalewska T, Zhou W (2014) Certified reference material IAEA-446 for radionuclides in Baltic Sea seaweed. Appl Radiat Isot 87:468–474